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Applied Research Laboratory

FINAL REPORT

Near Critical / Supercritical Carbon Dioxide Extraction for Treating Contaminated Bilgewater

PHASE 1

Partition Studies and Extraction Column Design

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EXECUTIVE SUMMARY

This report describes work performed at the Applied Research Laboratory of the Pennsylvania State University under Office of Naval Research Grant N00014-97-1-0353 covering the period from February 1997 to February 1999.

This study investigated the use of near critical / supercritical carbon dioxide (NC/SCCO₂) extraction as a method for removing oily and greasy contaminants from bilge water on deployed US Navy ships.

This report gives a brief discussion of the sources and composition of bilgewater, followed by an introduction to NC/SCCO₂ extraction technology and its use for water treatment. The results of a literature search are presented.

The ARL investigation concentrated on the following areas;

- Characterization of the effects of temperature, pressure and surfactant concentration on equilibrium partitioning of contaminants between the aqueous and NC/SCCO₂ phases.
- Development of techniques to defeat the detrimental effects of surfactants.
- Preliminary column sizing estimates based on the equilibrium partition data.

An extensive (99 tests) battery of partition coefficient measurements was performed. These experiments indicated that the presence of surfactants had a dramatic effect on equilibrium partitioning of contaminants, reducing the effectiveness of NC/SCCO₂ extraction by as much as two orders of magnitude.

It was discovered that the addition of small amounts of sodium chloride had the effect of largely reversing the deleterious effects of surfactants. In a practical shipboard system, seawater would be added to the untreated bilgewater to increase its salinity prior to NC/SCCO₂ extraction.

A series of preliminary column sizing estimates was performed, using HTU/NTU and flooding correlations developed for air stripping and liquid/liquid extraction. A notional 10 gallon-per-minute shipboard system would require a column with a total length of 24 feet, fabricated from 16" pipe.

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1. INTRODUCTION

All ships, commercial as well as military, produce bilgewater. This liquid waste has several sources, including;

- Leaks in shaft seals and/or through-hull fittings.
- Leaks (e.g. through valve packing) on fresh and salt-water piping systems.
- Water used for washing down equipment.
- Water used for fire prevention and/or fire-fighting operations onboard.
- Condensation of steam in machinery spaces.

Since this material contains a variety of contaminants, including organic materials and surfactants, it must be treated before being discharged overboard. While more recently commissioned ships tend to be “dryer,” resulting in lower waste volumes, the bilgewater in these newer vessels tends to have higher concentrations of contaminant materials.

While the composition of bilgewater varies between classes of ships, and can change with time depending on operational factors, measurements made on board the U.S.S. Carney (DDG 64) show levels (measured using both EPA 413.2 *oil and grease* and EPA 418.1 *petroleum hydrocarbon* methods) to be approximately 100 parts per million (ppm). (NRL, 1997).

In order to meet criteria set out in recent amendments to the International Convention for the Prevention of Pollution from Ships (MARPOL) treaty, the United States Navy has specified that oil and grease levels must be reduced to below 5 ppm before bilgewater is discharged overboard from its ships. Meeting these environmental requirements is essential in order that US Navy ships can continue to carry out their missions effectively throughout the world.

1.1 Current Treatment Processes

Historically, the Navy has relied on gravimetric separation to remove oily contaminants from bilgewater. Most ships contain one or more parallel plate treatment units, which use on the difference in density between oil and water to effect separation. Although these devices were designed to achieve a 15 ppm discharge level, there are a number of factors that can interfere with their operation.

First, ship motion continuously changes the orientation of the separator with respect to gravity, lowering the effectiveness of a separation process that relies on subtle differences in density to concentrate oily contaminants at the top of a contaminated water column. Second, some components of oily contaminants are actually soluble in water, and cannot be separated gravimetrically. This is particularly true of the lower molecular weight species, often known as the BTEX (Benzene, Toluene, Ethylbenzene, Xylene) fraction. Finally, contaminants can be adsorbed onto neutrally buoyant particles (such as

biological material) and be carried through the system along with the nominally treated water. (Rodriguez, 1997).

Biological growth is another problem that plagues current separator units. Because many bilgewater contaminants are somewhat biodegradable, anaerobic microorganisms grow in the separators. The resulting biological material can interfere with separator operation and make servicing of the units unpleasant because of their noxious waste products (e.g. hydrogen sulfide, or H₂S).

The study cited above found oil/water separator effluent levels on the USS Carney ranging from 29 to 73 ppm.

The Navy has investigated several new processes designed to operate as "polishers" downstream of the parallel plate units. A polymer adsorbent polishing unit has been installed on a number of DDG-51 vessels. These devices contain material that selectively adsorbs oils and greases. The USS Carney polisher units successfully treated the effluent from the parallel plate separators, resulting in effluent oil and grease levels of under 5 ppm in every case. (NRL, 1997).

A drawback to the use of these systems is that the adsorbents eventually become saturated with contaminants and must be replaced. The spent material must be stored on board and disposed of as hazardous waste when the ship returns to port.

More recently, an Ultrafiltration Membrane Polisher unit has been developed. This device apparently shows a great deal of promise as a next-generation secondary treatment system, although Rodriguez (1997-b) notes that the "Ultrafiltration Membrane Polisher (6.4) does not remove dissolved organics or contaminants <50 angstroms."

The technology of Near Critical / Supercritical Carbon Dioxide (NC/SCCO₂) Extraction has the potential to improve on conventional treatments and may offer advantages over the new secondary treatment systems discussed above. This technology will be introduced in more detail in the following section.

2: SUPERCRITICAL FLUIDS

Most materials can exist in several different physical forms, including the solid, liquid, and gas phases. The state of a pure material is governed solely by its temperature and pressure. Figure 1 is a phase diagram for carbon dioxide, showing the interrelationships between these conditions and the equilibrium state of carbon dioxide.

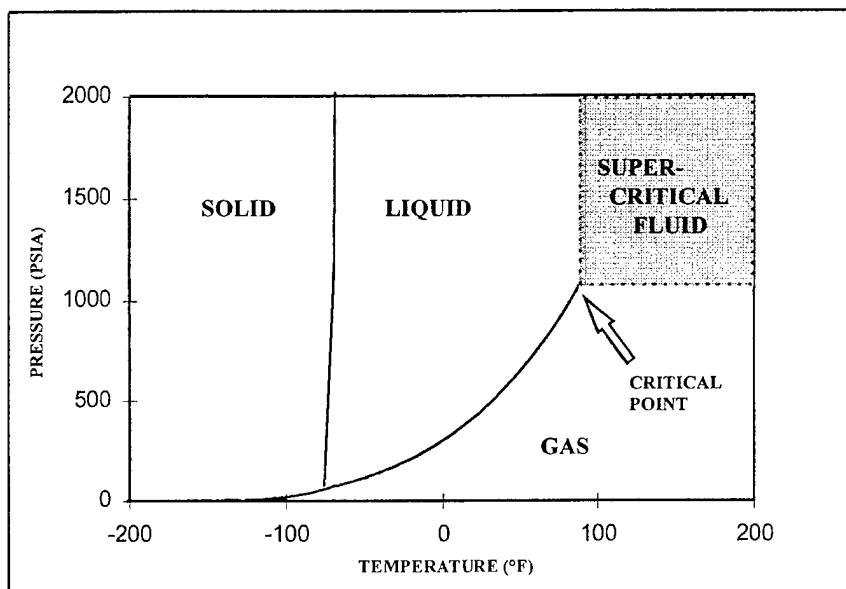


Figure 1: Carbon Dioxide Phase Diagram

The vapor pressure curve separates the liquid and gaseous regions. At temperature and pressure conditions that lie along this line, the material can exist as either a liquid or vapor, or both (i.e. a liquid stored under its own vapor pressure). Changes in temperature and pressure which take the species from conditions lying on one side of the line to the other result in a transformation from liquid to vapor or vice-versa. This causes sudden and discontinuous changes in the physical properties (i.e. density) of the species.

Note that the vapor pressure curve ends at the critical point; at temperatures and pressures above this point, there is no distinction between the liquid and vapor phases and the species is referred to as a supercritical fluid. Changes in temperature and pressure within this region result in dramatic but continuous changes in fluid properties. In addition, no phase changes will occur in this region (Van Wylen and Sonntag, 1978).

Supercritical fluids share some of the properties of both gases and liquids, as shown in Table 1, taken from Hoyer (1985). Like gases, supercritical fluids have very low viscosities and high diffusivities, and essentially no interfacial tension. These factors endow supercritical fluids with exceptional penetrating power. Hoyer indicates that "Because of their favorable mass transport properties, supercritical solvents allow a more

rapid approach to equilibrium, and they penetrate substrates more readily and deeper than do liquid solvents." Supercritical fluids have relatively high densities. The resulting increase in intermolecular forces causes these fluids to behave like liquids in terms of solvating power.

**Table 1: Comparison of Transport Properties of Liquids,
Gases and Supercritical Fluids**

Property	PHASE		
	Gas	Supercritical Fluid	Liquid
Density (gm/cm ³)	(0.6 - 2.0)10 ⁻³	0.2 - 0.9	0.6 - 1.6
Diffusion Coefficient (cm ³ /sec)	0.1 - 0.4	(0.2 - 0.7)10 ⁻³	(0.2 - 2.0)10 ⁻³
Viscosity (cp)	.01 - .03	.01 - .09	0.2 - 0.3

Carbon dioxide has emerged as the solvent of choice for most supercritical fluid processes. According to Taylor (1994), factors which make CO₂ attractive for use in supercritical fluid operations include;

- CO₂ is nontoxic
- Does not support combustion
- Exhibits readily attainable critical parameters
- Is commercially available in highly pure form
- Is environmentally friendly

At normal room temperatures, carbon dioxide is stored as a liquid under its own vapor pressure, which is 933 psi (6.43 MPa) at 77 °F (25 °C) (Matheson, 1974). As shown in Figure 1, these conditions lie very close to the critical point. For this reason, liquid carbon dioxide can be considered a "near critical" fluid.

Depending on the optimal process conditions, many applications take place under near critical conditions. To reflect the fact that carbon dioxide solvent operations occur over a wide range of temperatures and pressures, they will be referred to generically as "Near Critical / Supercritical Carbon Dioxide" (NC/SCCO₂) processes where appropriate for the remainder of this work.

Increasing concerns over environmental health and safety issues has led to the development of a wide range of techniques that use NC/SCCO₂ as a replacement for conventional chemical solvents. The most important example is decaffeination of green coffee beans. The Maxwell House division of the Kraft/General Foods Corporation operates an SCCO₂ plant in Texas that incorporates an extraction vessel approximately seven feet in diameter and seventy feet tall. This plant processes up to fifty million

pounds of coffee beans per year, replacing an older process that utilized the toxic and carcinogenic solvent methylene chloride.

In this process, supercritical carbon dioxide is used to selectively dissolve caffeine, while leaving the essential oils in place. Because SCCO₂ can penetrate deep within the bean to dissolve caffeine, it is not necessary to grind the coffee before processing. (McHugh and Krukonis, 1994).

NC/SCCO₂ has also been used to replace chemical solvents, such as Freon-113, for cleaning contaminated parts (Farncomb and Nauflett, 1994; Darvin and Hill, 1996), and as a replacement for perchloroethylene for dry cleaning of clothing (Betts, 1999).

In addition to its use as a replacement for conventional solvents, NC/SCCO₂ extraction is being investigated as a treatment technology for a number of polluted media. The following section describes NC/SCCO₂ water treatment processes.

3. NEAR CRITICAL / SUPERCRITICAL CARBON DIOXIDE WATER TREATMENT

Figure 2 is a schematic of a typical counterflow extraction apparatus for water treatment. In this device, contaminated wastewater flows downward through the extraction column, while the less dense NC/SCCO₂ phase flows upward. Mechanical agitation and/or packing material distributed through the column ensure adequate contact between the two phases.

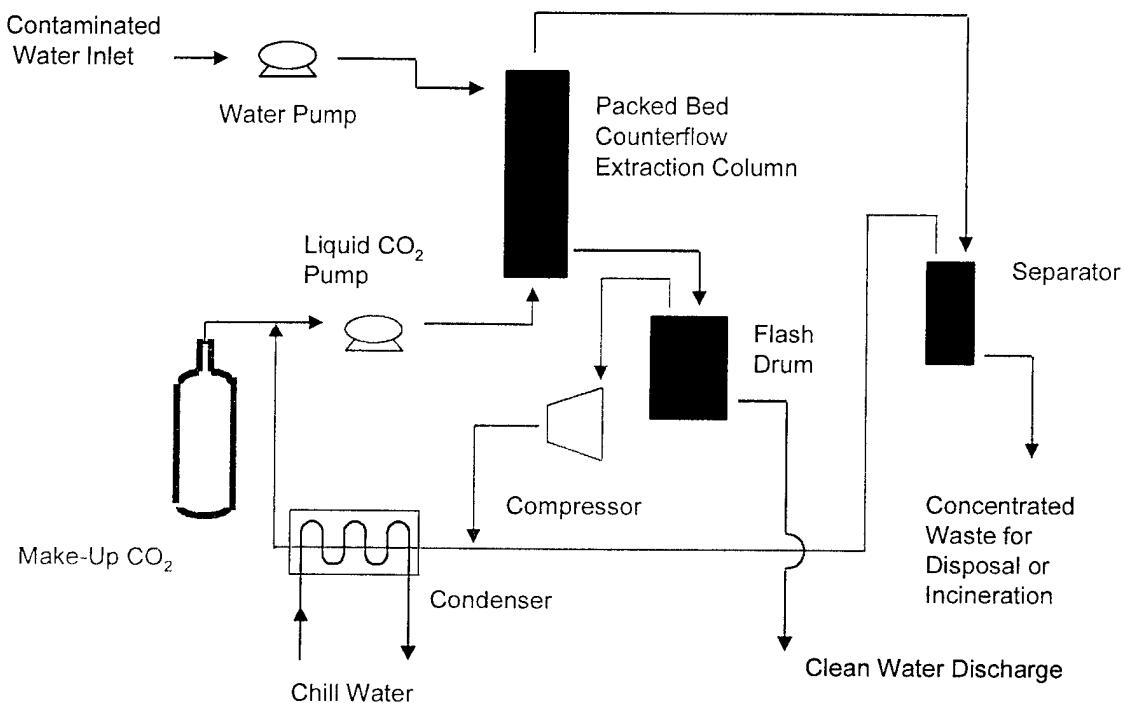


Figure 2: NC/SCCO₂ Extraction Apparatus for Water Treatment

Organic contaminants tend to concentrate in the carbon dioxide phase, and are carried out of the column by the CO₂. The carbon dioxide flows into a separator, where the pressure is reduced, causing the CO₂ to vaporize. The contaminant species, which are not soluble in the gas phase, fall out of solution and are collected in a highly concentrated form. The pure carbon dioxide is condensed to a liquid and recycled. A supply of CO₂ is carried to make up for losses, including carbon dioxide that dissolves in the aqueous phase and is carried out along with the treated water.

The contaminants are recovered in a highly concentrated form, suitable for incineration or handling as hazardous waste. Note that this waste stream is similar to the concentrated oil that is currently recovered from existing separators. Unlike incineration or supercritical water oxidation, NC/SCCO₂ extraction does not destroy contaminants.

3.1 Previous NC/SCCO₂ Water Treatment Studies

The use of critical/supercritical carbon dioxide for treatment of aqueous waste has been demonstrated in several pilot scale studies. Rice et. al. (1987) investigated the use of liquid (or near critical) CO₂ for extracting organic species from three aqueous industrial waste streams. The first waste investigated in this effort was sludge from a steel mill, containing approximately 30% solids by weight. Contaminants included oil and grease (6% - 30% of solids weight), iron fines and “toxic and non-toxic residues.” The second waste stream was a simulated pesticide processing residue, contaminated with mixed xylenes, carbon tetrachloride and “bottom sludge” containing solids, salts, carbon tetrachloride and “other insolubles.” The final test sample was a simulated waste stream from an acrylonitrile plant, containing acrylonitrile (250 ppm), acetonitrile (350 ppm), “non-toxic organics, ammonium ferrors and sodium sulfates (2.5 wt %).”

The results of this study were mixed. The steel mill sludge was difficult to process because of the presence of abrasive solids. Effective oil removal required very high solvent (CO₂) to feed ratios, making it difficult to justify the expense of this treatment process on the basis of the fuel value of the recovered oil. The carbon tetrachloride level in the simulated pesticide waste stream was reduced by 80%, but it proved more difficult to remove the xylene content. The contaminant levels in the final (acrylonitrile/acetonitrile) waste stream were reduced by over 99% (Rice et. al., 1987).

Farncomb and Nauflett (1995) describe the use of SCCO₂ for treatment of aqueous waste streams from energetic materials processing operations. Contaminants recovered from water included the nitrate esters Triacetin, Nitroglycerine, and Propylene Glycol Dinitrate (PGDN). Farncomb and Nauflett (1994) also indicate that their apparatus was used for extraction of “oils, greases and fats” from wastewater, but give no further information.

On a commercial scale, Clean Harbors, Inc. uses critical carbon dioxide to remove organic compounds (including alcohols, ketones, chlorinated solvents, and oils) from as much as 35,000 gallons of contaminated wastewater on a daily basis. The treated water has BTEX concentrations below 5 ppm, allowing discharge to a municipal waste water treatment plant. Waste streams containing as much as 30% of the following contaminants have been successfully treated (Clean Harbors: Swab, 1995-1998);

- Isopropanol, butanol, and other higher molecular weight alcohols
- Acetone and other ketones
- Halogenated organics such as carbon tetrachloride, methylene chloride, and chloroform
- Aromatics (benzene, toluene, ethylbenzene, xylenes)

The Clean Harbors extraction column is 32 feet high, with a diameter of 2 feet (Black, 1996).

4. NC/SCCO₂ EXTRACTION FOR BILGEWATER TREATMENT

The remainder of this document describes a study, performed at The Applied Research Laboratory of the Pennsylvania State University (ARL/PSU), which explored the use of near critical / supercritical carbon dioxide extraction for removing oily and greasy contaminants from bilgewater on deployed US Navy vessels.

The use of NC/SCCO₂ extraction may offer several advantages relative to existing bilgewater treatment systems. First, the process should be effective for removing even soluble contaminants, unlike the new ultrafiltration system used for secondary treatment. Second, unlike polymer adsorbent secondary treatment units, there should be no need for manual changeout of expendables. The cylinders of make-up CO₂ would be installed on a manifold before the ship leaves port, and replaced at the end of the deployment. Finally, the waste should be collected in a very concentrated form, suitable for incineration (on-board or in port), reducing handling and logistic concerns.

This empirical program was funded by the Office of Naval Research under grant N00014-97-1-0353. The period of performance was February 1997 through February, 1999.

The investigation originally focused on the following areas;

- Demonstration and characterization of the counterflow extraction process, including the effects of temperature, pressure, agitation and column geometry.
- Evaluation of the effects of surfactants on the extraction process, and development of techniques to reduce surfactant interference.

As will be discussed in the following sections, the program ultimately evolved (with sponsor approval) into a study that encompassed;

- Characterization of the effects of temperature, pressure and surfactant concentration on equilibrium partitioning of contaminants between the aqueous and NC/SCCO₂ phases.
- Development of techniques to defeat the detrimental effects of surfactants.
- Preliminary column sizing estimates based on the equilibrium partition data.

4.1 ARL Batch Extraction Studies

One of the primary factors governing the performance of any extraction process is the relative affinity of the solute (in this case, the oily and greasy contaminant materials) for the various phases present in the extraction process.

In the case of NC/SCCO₂ bilgewater treatment, this metric is referred to as the partition coefficient, K_{CO₂}, which can be defined as;

$$K_{CO_2} = \frac{C_{CO_2}}{C_{H_2O}}$$

The partition coefficient is a nondimensional number that represents the ratio of the concentration of contaminant in the carbon dioxide phase to that in the liquid phase, once equilibrium has been reached. The partition coefficient is a function of a wide range of process variables such as pressure, temperature and surfactant concentration.

The physical significance of the partition coefficient is that it represents the degree to which the contaminants tend to concentrate in the carbon dioxide extraction solvent as opposed to the aqueous phase. Higher values of K_{CO₂} indicate that the contaminant is more likely to move from water to NC/SCCO₂, obviously a desired result.

In practice, partition coefficient data such as K_{CO₂} is one of the fundamental variables required in order to design extraction processes. Given this equilibrium data, one can determine the relative amount of extraction solvent (CO₂) that is theoretically needed to obtain a desired effluent level. Higher K_{CO₂} values reduce the amount of carbon dioxide that is required to treat a given amount of contaminated water.

The first portion of the ARL empirical investigation focused on determining the effects of process variables, notably temperature, pressure and surfactant concentration, on the equilibrium partition coefficient K_{CO₂}. The most detailed discussion of the methodologies applied is contained in the Masters thesis Near Critical / Supercritical Carbon Dioxide Extraction of Oil From Ship Bilgewater (Swab, 1997), which is included in its entirety as Appendix A of this report.

Partition studies were performed in batch mode using the apparatus shown in Figure 3, a model SFT-1000 general purpose extraction system developed by Supercritical Fluid Technologies, of Newark Delaware. More details are given in Appendix A.

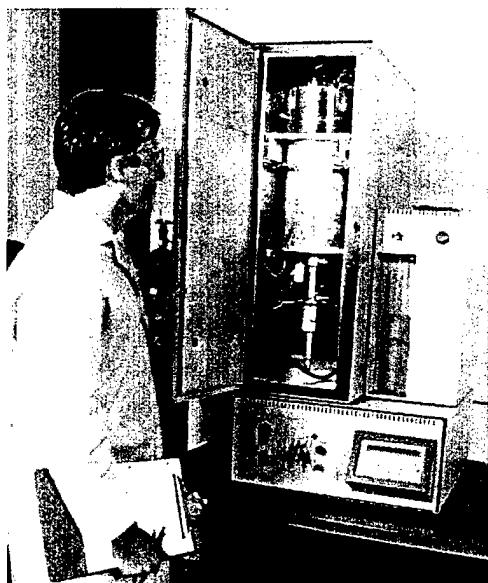


Figure 3: NC/SCCO₂ Apparatus Used in Batch Partition Studies

To summarize the procedures discussed in Appendix A, extraction tests consisted of the following steps;

1. Place a known quantity of simulated bilgewater in the pressure vessel of the NC/SCCO₂ extraction system.
2. Bring the system to the desired process conditions (pressure and temperature).
3. Use magnetically coupled impeller system to agitate the bath, enhancing contact between the NC/SCCO₂ and aqueous phases. Allow the system to reach equilibrium.
4. Turn off impeller, allowing carbon dioxide and aqueous phases to separate.
5. Draw a sample of "treated" water (raffinate) from the bottom of the vessel.
6. Analyze sample using Fourier Transform Infrared Spectroscopy to determine residual oil content. Calculate K_{CO₂}.

In consultation with the Naval Surface Warfare Center - Carderock Division (NSWC-CD), a model bilgewater consisting of 300 ppm of an oil mixture (DTRC Oil Mix #4) and, in some cases, 25 ppm of a surfactant mixture (DTRC Detergent Mix #4) was selected for this study. Table 2 lists the compositions of these mixtures, which are used as standards for evaluating bilgewater treatment systems. (NSWCCD, 1997).

Table 2: Composition of Simulated Bilgewater Constituent Mixtures

DTRC Oil Mix #4		DTRC Detergent Mix #4	
Constituent	Weight Percentage	Constituent	Weight Percentage
Diesel Fuel Marine MIL-F-16884H	50%	Type 1: General Purpose Detergent MIL-D-16791	50%
2190 TEP Steam Lube Oil MIL-L-17331H	25%	Commercial Detergent: Liquid Tide	25%
9250 Diesel Lube Oil MIL-L-9000H	25%	Cleaning Solvent PD-680A, Type 2	25%

Although the 300 ppm oil concentration chosen for this study is somewhat higher than that found in typical bilgewater, NSWC-CD personnel felt that the more challenging condition would give an indication of the ability of NC/SCCO₂ extraction to function during a "worst-case" scenario, such as the aftermath of a large spill of oil in the bilge (Rodriguez, 1997).

In addition, four tests were performed using AFFF (Aqueous Film Forming Foam) as a surfactant in place of DTRC Detergent Mix #4. The effects of AFFF were found to be less significant than those of the standard surfactant mixture.

The conclusions of the first phase of the research (extending through the end of calendar year 1997) were as follows;

1. The presence of even small amounts of surfactant has a dramatic effect on partition behavior. The addition of 25 ppm of DTRC Detergent Mix #4 lowered measured K_{CO₂} values by two orders of magnitude.
2. While the partition coefficient is affected by pressure and temperature, it appears that (over the pressure range investigated in this effort), intermediate pressures (e.g. 1000 psi) resulted in K_{CO₂} values as high as those obtained under higher pressure (e.g. 1200 psi) conditions.
3. Surprisingly, partition coefficient values obtained at near critical (i.e. liquid) conditions are as high as those measured under warmer supercritical conditions.

Given the primary finding, i.e. that surfactant effects were so dramatic, it was decided to re-focus the program on methods to defeat the effects of surfactants. With the approval of the sponsor (Guard, 1997), the goal of testing a model counterflow system was shelved in favor of additional partition characterization studies.

Tests performed through July 1998 focused on evaluating techniques to limit the effects of surfactant interference on the extraction process. A number of chemical additives, known to interfere with surfactant action by disrupting micelle formation, were added to the bilgewater. Additives tested in this effort included butanol (Kahlweit et. al, 1991), sodium citrate, sodium chloride, and ASTM standard artificial seawater.

4.2 Batch Extraction Study Results

The results of all 99 extraction tests are summarized in Table 3. Appendix A includes a detailed discussion of the analytical procedures and calculations used to derive the values in this table.

Table 3: Results of Bilgewater Extraction Tests Through July, 1998

Run#	T (C)	P (psi)	Deterg.	AFFF	Additive	Initial	Raw	Raff.	K _{CO2} I	K _{CO2} R.
*7	27	900	0	0	0	464	363	2.53	391	306
*8	27	1019	0	0	0	465	363	3.45	287	224
*9	27	1235	0	0	0	467	346	7.31	135	99
11	33	1123	0	0	0	464	371	13	74	59
*12	33	1318	0	0	0	456	431	20.2	34	32
14	26	896	23	0	0	469	409	191	3.12	2.45
15	34	1455	0	0	0	473	390	6.71	149	123
16	39	1272	0	0	0	471	363	4.4	227	175
17	40	1484	29	0	0	464	354	199	2.86	1.67
18	39	1229	0	0	0	450	364	4.17	229	185
19	39	1479	0	0	0	460	381	4.88	200	165
20	33	1294	21	0	0	467	380	148	4.62	3.36
21	33	1092	28	0	0	477	404	209	2.75	2
22	34	1485	21	0	0	462	380	170	3.68	2.65
23	39	1185	28	0	0	467	396	232	2.17	1.52
24	39	1288	22	0	0	459	413	187	3.12	2.59
25	30	1027	27	0	0	461	379	195	2.93	2.02
26	28	1189	22	0	0	469	423	158	4.22	3.6
27	26	890	0	0	0	469	375	6.08	163	130
28	34	1466	0	0	0	505	442	4.66	230	201
29	40	1153	0	0	0	465	375	12.4	78	63
30	28	1192	21	0	0	461	401	158	4.11	3.3

Table 3, Continued

Run#	T (C)	P (psi)	Deterg.	AFFF	Additive	Initial	Raw	Raff.	K _{CO₂} I	K _{CO₂} R.
31	34	1278	24	0	0	465	416	174	3.59	2.98
32	40	1279	23	0	0	460	382	171	3.63	2.65
34	40	1129	0	0	0	459	340	7.12	136	100
35	28	913	0	0	0	477	369	9.92	101	78
37	27	1185	30	0	5wt%Cit.	478	324	6.42	158	106
*38	32	1300	25	0	5wt%Cit.	454	317	7.28	132	91.3
39	27	1196	25	0	2wt%But.	483	334	42.1	22.5	14.9
40	34	1232	27	0	2wt%But.	474	336	28.6	33.4	23.1
41	27	1175	25	0	1wt%Cit.	460	262	5.6	174	98
42	27	1170	27	0	0.5wt%Cit.	471	349	8.18	121	89
43	27	1177	25	0	0.1wt%Cit.	461	382	36.3	25	20
44	34	1275	22	0	0.5wt%Cit.	465	332	6.16	160	113
45	34	1302	23	0	0.1wt%Cit.	461	365	32.2	29	22
46	27	1230	27	0	5wt%NaCl	462	367	7.89	123	97.6
47	27	1173	25	0	1wt%NaCl	463	386	5.13	191	159
48	27	1195	21	0	0.5wt%NaCl	475	344	5.11	197	142
49	27	1174	25	0	0.1wt%NaCl	465	414	26.6	35.4	31.2
50	33	1278	28	0	1wt%NaCl	484	360	10.7	94.9	70.2
51	33	1277	25	0	0.5wt%NaCl	453	343	15.4	60.9	45.6
52	33	1275	27	0	0.1wt%NaCl	468	438	107	7.24	6.64
54	27	1203	101	0	0.5wt%NaCl	463	375	83.5	9.75	7.49
55	27	1202	46	0	0.5wt%NaCl	470	371	7.77	127.6	100.3
56	27	1204	101	0	1wt%NaCl	454	368	39.8	22.3	17.7
57	27	1205	102	0	1.5wt%NaCl	472	378	23.1	41.7	33
58	27	1208	100	0	2wt%NaCl	470	396	20.7	35.5	29.6
59	27	1204	101	0	2.5wt%NaCl	472	366	20.9	46.3	35.2
60	27	1201	124	0	2wt%NaCl	470	385	43.7	35.4	28.7
61	27	1229	53	0	1wt%NaCl	475	418	5.49	183	161
62	27	1197	77	0	0.5wt%NaCl	475	415	31.8	36.2	31.3
63	27	1209	78	0	1wt%NaCl	457	389	18.8	50	42.2
64	27	1224	79	0	1.5wt%NaCl	468	364	10.9	89.9	69.5
65	27	1198	0	43	0	466	422	9.04	108	98
66	27	1197	0	96	0	476	440	20.8	46.9	43.2
67	27	1209	0	256	0	471	422	26.4	36.1	32.1
68	27	1196	0	263	0.5wt%NaCl	477	416	22	44.4	38.4
69	29	1206	0	0	0	470	400	4.85	206	175
70	38	1215	0	0	0	465	390	3.21	309	258
71	27	1208	0	0	0	457	388	5.46	177	150
72	27	1208	0	0	0	452	364	3.46	278	223
73	27	1016	0	0	0	467	387	2.93	340	281

Table 3, Continued

Run#	T (C)	P (psi)	Deterg.	AFFF	Additive	Initial	Raw	Raff.	K _{CO₂} I	K _{CO₂} R.
75	27	1030	0	0	0	470	404	4.16	240	206
76	27	923	0	0	0	477	401	7.06	143	120
77	27	1231	31	0	0.5wt%NaCl	475	405	11.9	83.47	70.86
78	27	1233	27	0	0.5wt%NaCl	470	399	17.4	55.79	47.04
79	28	1220	26	0	0.5wt%NaCl	463	393	21.9	43.20	36.35
80	27	1007	27	0	0.5wt%NaCl	457	376	70.8	11.70	9.25
81	28	1216	27	0	1.0wt%NaCl	469	378	29.2	32.31	25.62
82	28	1166	27	0	0.5wt%NaCl	467	371	14.9	65.08	51.26
83	27	1182	26	0	0.5wt%NaCl	466	412	30.9	30.20	26.45
84	27	1189	26	0	0.5wt%NaCl	459	378	13.5	70.78	57.91
85	28	1186	32	0	0.5wt%NaCl	467	396	9	109.15	92.23
86	28	1184	26	0	0.5wt%NaCl	454	374	7.8	122.70	100.70
87	28	1185	26	0	0.5wt%NaCl	457	380	9.6	99.96	82.76
88	27	1183	24	0	1.0wt%NaCl	462	367	10.9	88.77	70.07
89	28	1180	27	0	1.0wt%NaCl	463	388	10.3	94.27	78.65
90	28	1192	28	0	1.0wt%NaCl	461	405	8.19	118.59	103.92
91	28	1199	27	0	1.0wt%NaCl	460	400	8.98	107.73	93.40
92	27	1188	26	0	1.0wt%NaCl	462	359	5.54	176.73	136.85
93	28	1199	26	0	1.0wt%NaCl	464	387	7.23	135.51	112.67
94	28	1185	28	0	43%Seah2O	469	369	6.15	161.43	126.55
95	27	1185	27	0	30%Seah2O	469	397	6.09	163.04	137.68
96	28	1182	28	0	30%Seah2O	465	382	9.28	105.33	86.15
97	27	1173	25	0	30%Seah2O	463	411	7.69	127.00	112.49
98	27	1196	29	0	30%Seah2O	465	405	10.7	91.07	79.04
99	27	1192	24	0	30%Seah2O	466	395	5.68	173.83	147.02

** Indicates Failure of Data Acquisition System. Data logged by hand.

In general, the polar additives (sodium citrate, sodium chloride, sea-salt) were largely effective at defeating surfactant effects. Although the exact mechanism for this process is unknown, it is probably related to the well-known “salting out” phenomenon, in which ionic species always decrease the aqueous solubility of neutral nonpolar compounds (Schwartzbach, et. al., 1993).

Figure 4 is a comparison of raw bilgewater and the treated raffinate obtained in batch testing. Note that the treated water is noticeably clearer. Figure 5 summarizes the results of the batch experiments. Note that each K_{CO₂} data bar represents the aggregate result of a number of individual extraction experiments.

4.3 Conclusions of Batch Extraction Study

The conclusions of the batch extraction portion of this program are summarized below.

1. The presence of even small amounts of surfactants interferes significantly with NC/SCCO₂ extraction of oily contaminants from simulated bilgewater.
2. Addition of traces of ionic species (e.g. 1% NaCl) can largely offset the detrimental effects of surfactants.
3. In a shipboard system, addition of seawater to the raw bilgewater feed (approximately 30% seawater by volume for bilgewater that is non-saline) should allow NC/SCCO₂ to effectively extract oily contaminants from bilgewater.

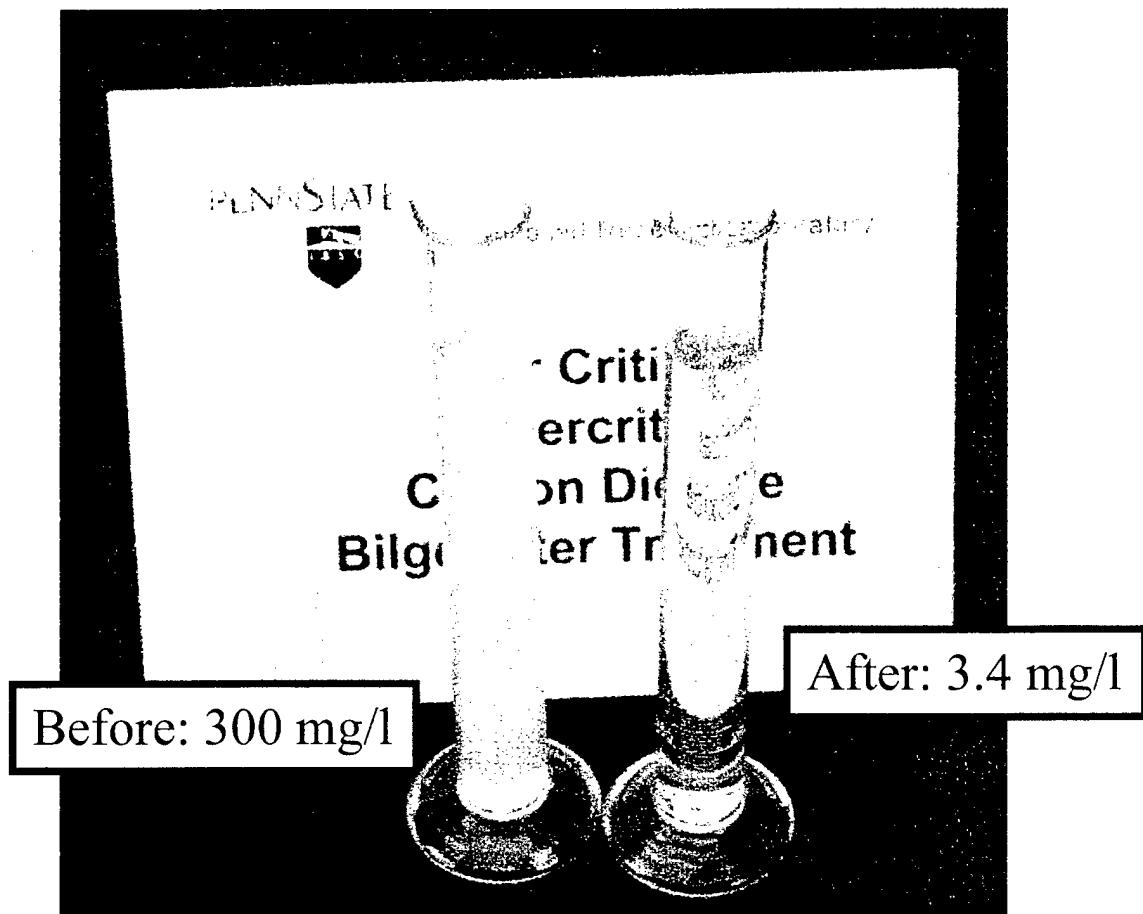
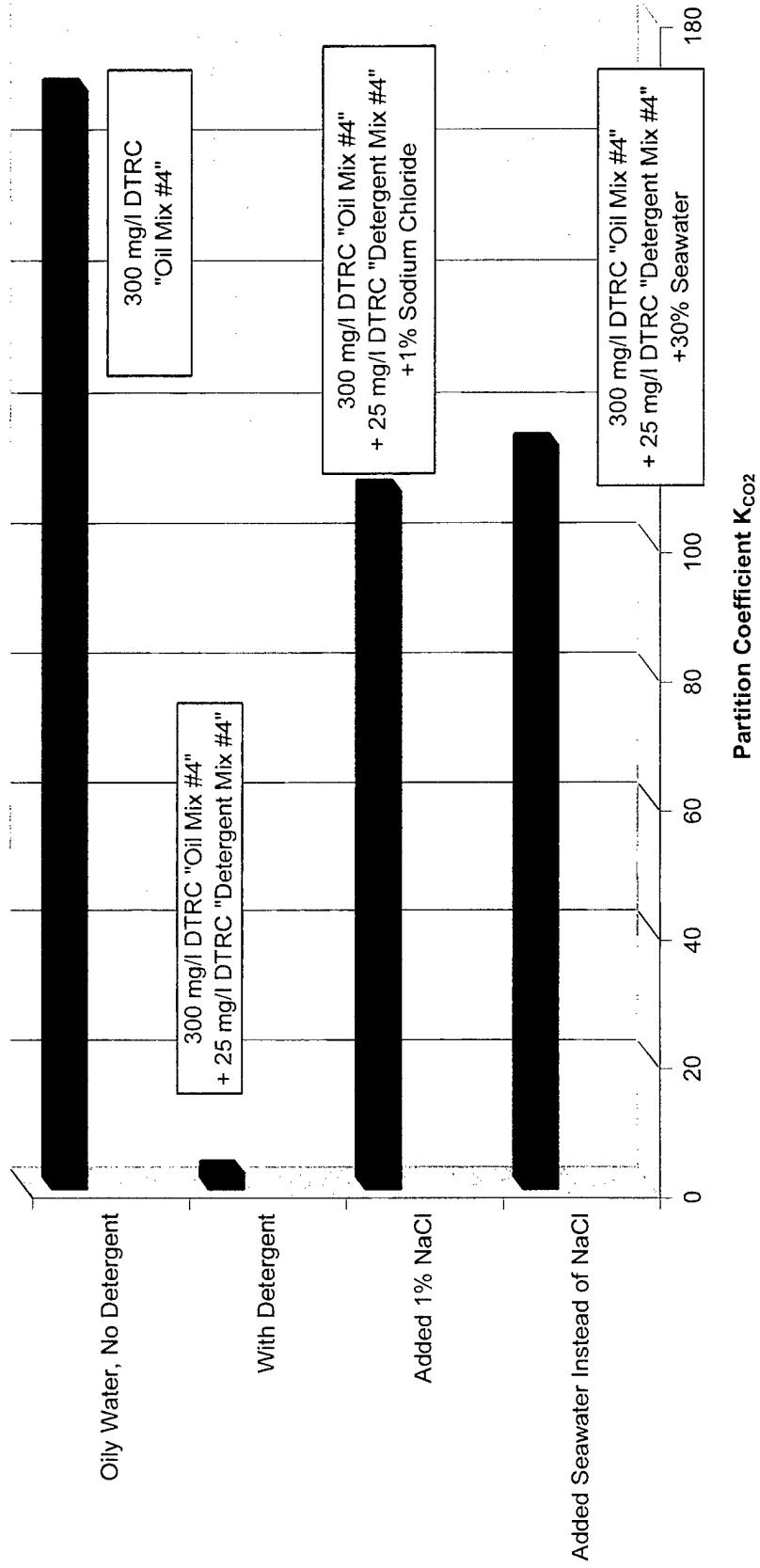


Figure 4: Comparison of Raw Bilgewater and Treated Raffinate

Figure 5: Summary of Batch Extraction Results



5. PRELIMINARY DESIGN OF COLUMN FOR BILGEWATER TREATMENT

Having determined that NC/SCCO₂ can extract oily contaminants from bilgewater, and that addition of seawater to the raw bilgewater feed can effectively eliminate the deleterious effects of surfactants, an attempt was made to develop a preliminary design for shipboard integration.

As discussed in a previous section, a number of empirical studies have evaluated the use of NC/SCCO₂ for removing organic contaminants from wastewater. Unfortunately, no process design data is available from the scientific or engineering literature. Although a commercial system is in operation at this time, details of the column's internal configuration are proprietary.

An attempt was made to size a column using several standard design tools originally developed for liquid-liquid extraction and for air stripping operations. The use of these correlations was justified on the basis of the fact that the physical and transport properties of NC/SCCO₂ are intermediate between those of liquids and gases (see Table 1). Details of these calculations are given in Appendix B.

To summarize the results of Appendix B, a notional shipboard extraction column designed to treat 10 gallons per minute of contaminated bilgewater should require a column consisting of a total of 24 feet of 16" pipe.

Several ARL personnel visited Ingalls Shipbuilding, of Pascagoula Mississippi, to tour the USS Porter (DDG78) which was under construction at the time. Measurements were taken of the equipment space currently devoted to the oil water separator equipment. Figure 6 shows two views of the current bilgewater treatment system as installed on the Porter.

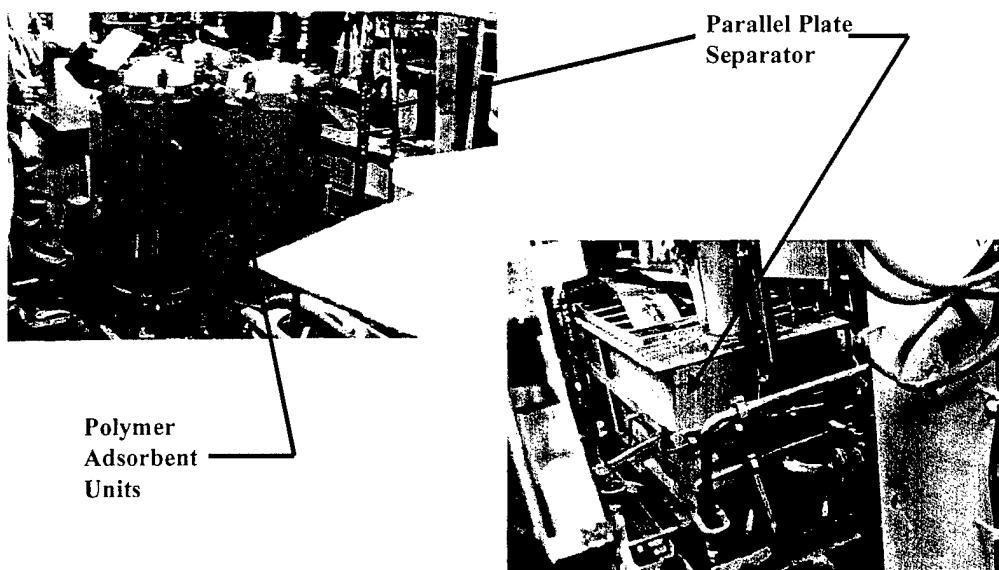


Figure 6: Bilgewater Treatment System on DDG-51 Class Ships

A preliminary layout was developed using the results of the column design analyses discussed in Appendix B. Using representative Commercial Off The Shelf (COTS) compressors, condensers, and pumps, it was determined that the notional 10 gpm NC/SCCO₂ system could be configured to fit on a 100" by 100" pallet. This is considerably larger than the existing system, which occupies a footprint of approximately 70" by 80". It is anticipated that with optimized components and packaging, the size of the extraction system could be reduced.

Figure 7, below, shows this preliminary layout, compared to the current system footprint.

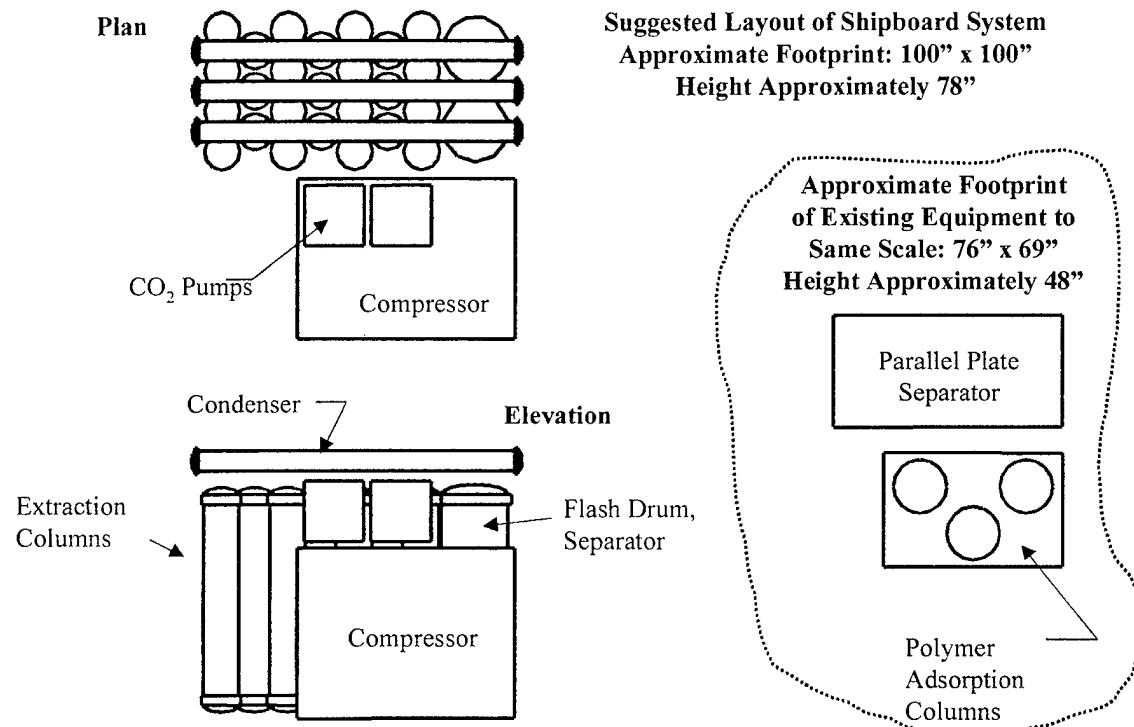


Figure 7: Preliminary Layout for Notional 10 gpm Shipboard System.

6. CONCLUSIONS, RECOMMENDATIONS FOR FUTURE WORK

Batch partition studies indicate that the addition of seawater can largely defeat the effects of surfactants when near critical / supercritical carbon dioxide is used to extract oils and greases from aqueous solutions. This makes NC/SCCO₂ technology a potentially viable option for treating bilgewater prior to discharge from deployed Navy fleet units.

Preliminary analyses indicate that a column with an overall height of 24 feet, fabricated from 16 inch diameter pipe, would be required to treat a 10 gallon per minute flow. This is considerably larger and heavier than current systems, which consist of a parallel plate separator with a secondary "polishing" unit (polymer adsorption or ultrafiltration). It is anticipated that an optimized NC/SCCO₂ design would be somewhat smaller.

In order to verify the effectiveness of the design tools used for the preliminary column size estimates, it will be necessary to construct and test a laboratory scale counterflow extraction system. Such a system has been constructed under a new ONR grant (N00014-99-1-0421). Its operation is currently being evaluated.

APPENDIX A: MASTERS THESIS BY CHRISTOPHER L. SWAB

The Pennsylvania State University

The Graduate School

THE EFFECTS OF TEMPERATURE,
PRESSURE, AND DETERGENT ON
CARBON DIOXIDE EXTRACTION
OF OIL FROM WATER

A Thesis in
Environmental Pollution Control

By

Christopher L. Swab

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Submitted in Partial Fulfillment
Of the Requirements
For the Degree of

Master of Science

December 1997

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ABSTRACT

This thesis is part of a long-term study of the viability and design of a shipboard near critical* or supercritical carbon dioxide system to be used for the remediation of bilge water. The topic of this thesis is an investigation into the ability of near critical and supercritical carbon dioxide (NC/SCCO₂) to remove approximately 300 mg/L oil from water. The general objective of this study was to conduct a proof-of-concept investigation of NC/SCCO₂ extraction of oil from prepared samples representing bilge water. Specifically, the research objectives included the following:

- to investigate the potential of NC/SCCO₂ for the extraction of oil from model bilge water, using a batch reactor (static system, impeller mixing);
- to investigate the effect of pressure variation within three temperature ranges on the efficiency of carbon dioxide extraction of oil from bilge water.
- to determine the effect of detergent on the NC/SCCO₂ extraction process.

In batch tests of oil and water only, partition coefficients for oil between carbon dioxide and water (K_{CO_2}) were in the range of 32 (33°C, 1300 psi) to 224 (24°C, 1000 psi). Extraction efficiency of the system decreased greatly when detergent was added to the samples. K_{CO_2} ranged from 1.5 (40°C, 1180 psi) to 3.6 (28°C, 1190 psi) after the addition of approximately 25 mg/L detergent.

*Defined as liquid carbon dioxide at near critical temperature and pressure.

Polynomial regression “best fit” lines for all batch groups were not linear, but showed either convex or concave curvature, depending upon the pressure at which the highest K_{CO_2} value occurred for each batch test group. In non-detergent tests, this may have been due to the effects of pressure variation on the solvating power of the CO_2 . In detergent tests, this may have been caused by the effects of pressure variation on the surfactant micelle, or possibly by the detergent mix used in this study, should the mix contain ionic and nonionic detergents.

Best fit lines for K_{CO_2} values calculated using initial mix concentrations of oil paralleled best fit lines for K_{CO_2} values calculated using raw concentrations closely, but were greater in value since initial concentrations of oil were greater than raw concentrations of oil for each batch test.

Impeller mixing efficiency during the creation of the bilge water models remained reasonably constant throughout the study, despite variations in initial oil concentration, amount of detergent, and temperature for batch tests. K_{CO_2} values were shown to increase only slightly during a 13 hour time period after raffinate sampling for detergent tests.

If NC/SCC CO_2 extraction is to be considered as a viable method of removing oil from bilge water containing detergents, further research will be needed on methods of breaking surfactant micelles before or during the extraction process.

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GLOSSARY

- ***Critical density (ρ_c)***
Density of a supercritical fluid at its critical temperature and critical pressure.
- ***Critical point (C_p)***
The characteristic temperature (T_c) and pressure (P_c) above which a gas cannot be liquefied.
- ***Critical pressure (P_c)***
The minimum pressure needed to liquefy a substance at its critical temperature.
- ***Critical temperature (T_c)***
The maximum temperature at which a gas can be liquefied by an increase in pressure.
- ***Microemulsion***
Thermodynamically stable solutions generally containing water, a surfactant, and an oil.
- ***Raffinate samples***
Model bilge water samples that have been extracted (cleaned) by carbon dioxide at elevated temperatures and pressures.
- ***Raw samples***
Model bilge water samples prepared by impeller mixing for this study.
- ***Reduced density (ρ_r)***
The ratio of density in the system to the critical density (ρ_c). $\rho_r = \rho / \rho_c$
- ***Reduced pressure (P_r)***
The ratio of the pressure in the system (P) to the critical pressure (P_c). $P_r = P / P_c$
- ***Reduced temperature (T_r)***
The ratio of the temperature (T) in the system to the critical temperature (T_c). $T_r = T / T_c$
- ***Supercritical fluid***
The defined state of a compound, mixture or element above its critical pressure (P_c) and critical temperature (T_c).

All definitions except raw and raffinate samples from Taylor, 1996, and Beckman et al., 1991.

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Chapter 1

INTRODUCTION

Statement of Problem

Due to current treatment inadequacies and anticipated changes in prevailing global discharge standards, remediation of bilge water is an ongoing concern for the United States Navy. Bilge water is generated from a variety of sources, including engine room washdown, leakage from valve packing, and condensate from escaping steam. As a result, bilge water may be contaminated with particulate matter, metals, and most typically, hydrocarbons and detergents. The hydrocarbons, which are a mixture of machining and lubricating oils, are found both as a floating free oil layer and emulsified in the bilge water itself.

At present, the USN employs parallel plate oil/water separators (OWS) to remove 90% of the free oil found in bilge water. Since current standards dictate that oil levels be below 5 mg/L before bilge water may be discharged, the Navy also employs an ultrafiltration membrane unit to remove (or “polish”) the remaining oil contamination. Unfortunately, the membrane polishing unit does not remove dissolved organics or contaminants less than 50 angstroms in size, and resulting oil contamination in the field may be as high as 300 mg/L.

One of the methods the USN is currently investigating to replace the membrane filtration process is carbon dioxide extraction. Near critical / supercritical carbon dioxide

extraction may have the potential to remove oil contamination in bilge water from 300 to less than 5 mg/L. To meet the needs of the USN, the treatability of bilge water by carbon dioxide extraction was determined in this study.

Objectives

The general objective of this study is to conduct a proof-of-concept investigation of the use of near critical / supercritical carbon dioxide extraction for removing oil from samples of bilge water prepared based on USN specifications. Specifically, the research objectives included the following:

1. To investigate the potential of near critical / supercritical carbon dioxide (NC/SCCO₂) to remove oil from bilge water, using a batch reactor.
2. To investigate the effect of pressure variation within three temperature ranges on the efficiency of carbon dioxide extraction of oil from bilge water.
3. To evaluate the effects of surfactants on the extraction process.

Chapter 2

THEORY OF NC/SCCO₂ EXTRACTION

Near Critical and Supercritical Carbon Dioxide

Figure 1 is a pressure-temperature diagram for carbon dioxide. At 31.06°C and 1070 psi is the critical point (C_p), beyond which CO₂ is neither a liquid nor a gas, but exhibits properties of both. The defined state of CO₂ beyond its C_p is known as the supercritical fluid state. At pressures above the vapor pressure curve (boiling line), and temperatures close to, but not above the critical temperature (T_c), CO₂ is in a near critical (liquid) state.

Raising the density of CO₂ increases its solvating power by augmenting the intermolecular forces of the CO₂. However, supercritical (SC) CO₂ may not necessarily be in a more dense state than near-critical (NC) CO₂. **Table 1** gives a temperature-pressure-density relationship for CO₂ at near-critical and supercritical temperatures and pressures. The effects of raising temperature and pressure to C_p and beyond can be seen when comparing densities within the supercritical (shaded) region to those of the near-critical (non-shaded) region. Although density increases with pressure for each temperature, it decreases with temperature for each pressure. Therefore SCCO₂ at high temperatures and low pressures may be less dense than NCCO₂ at high pressures and low temperatures. The effects of temperature increase on the density of CO₂ can also be seen in **Figure 2**, which shows isotherms for CO₂ at given temperatures within pressure ranges in the near-critical and supercritical region.

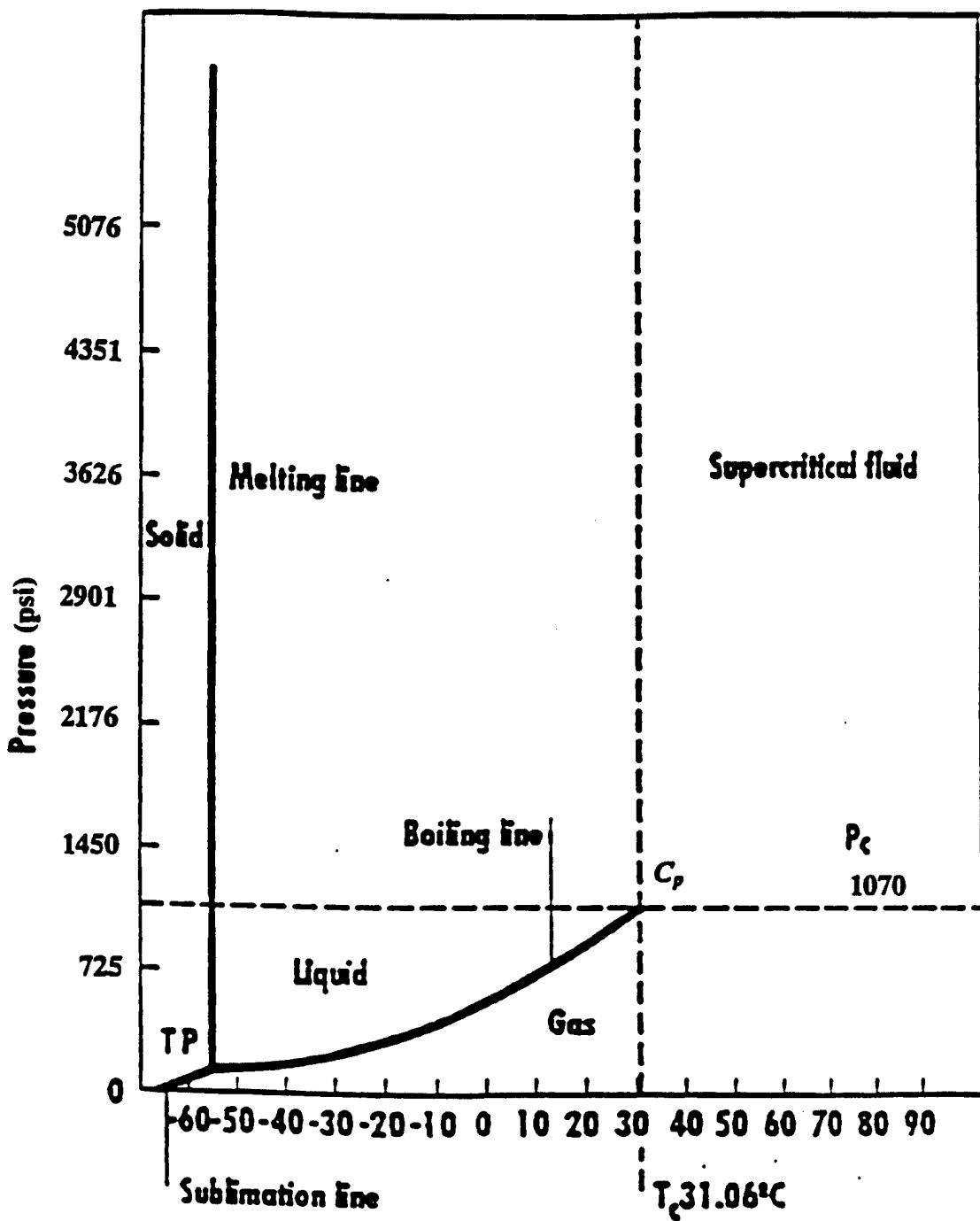


Figure 1: Pressure – temperature diagram for carbon dioxide.
Adapted from Taylor, 1996.

Table 1: Temperature-pressure-density relationship for CO₂. Density is given in g/mL.
 note: Temperature and pressure ranges are those used in the study. Shading denotes density in the supercritical region. * denotes critical density, ρ_c

T (C)	900psi	1000psi	1070psi	1100psi	1200psi	1300psi	1400psi	1500psi
24	0.233	0.417	0.777	0.784	0.806	0.826	0.852	0.874
26	0.222	0.398	0.743	0.752	0.78	0.804	0.82	0.834
28	0.213	0.38	0.704	0.716	0.751	0.781	0.801	0.818
30	0.201	0.331	0.536	0.563	0.658	0.754	0.78	0.802
31.1	0.195	0.309	*0.472	0.502	0.615	0.74	0.768	0.794
32	0.188	0.278	0.387	0.418	0.553	0.724	0.753	0.781
34	0.175	0.227	0.275	0.305	0.45	0.689	0.722	0.752
36	0.169	0.213	0.251	0.278	0.41	0.628	0.675	0.721
38	0.163	0.202	0.236	0.26	0.374	0.555	0.621	0.69
40	0.159	0.195	0.225	0.245	0.388	0.475	0.559	0.658

note: This table was calculated using *SF-Solver Software for Supercritical Fluid Analysis*, 1991.

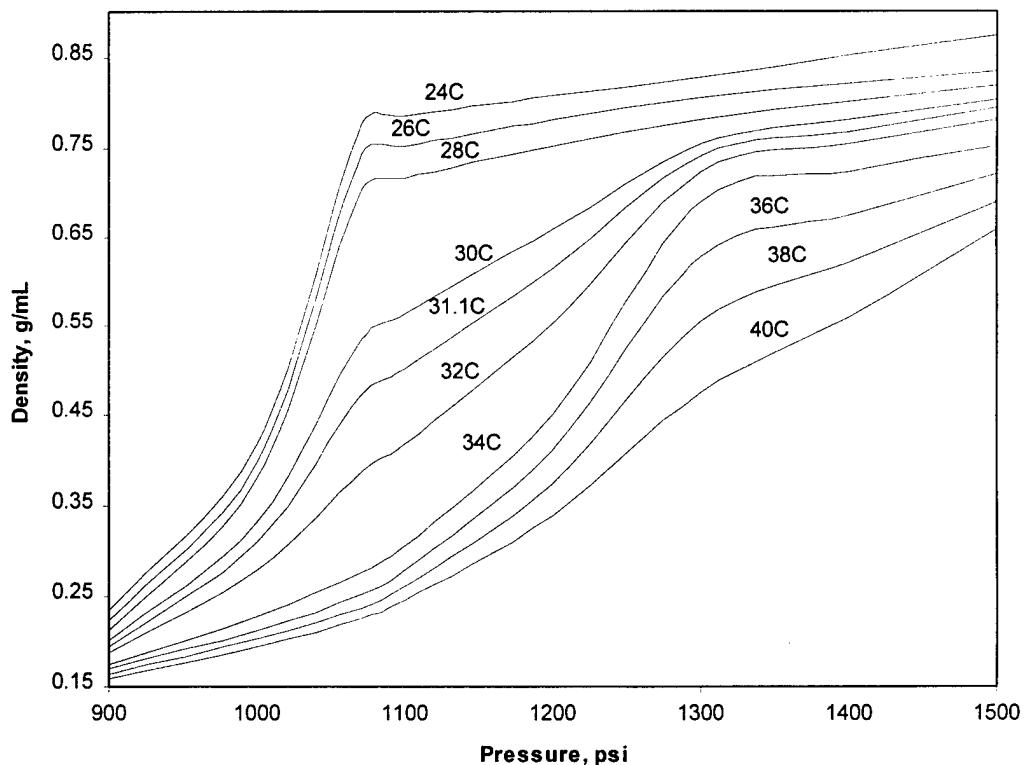


Figure 2: Density vs. pressure for CO₂ at various temperatures.

Figure 3 is a reduced pressure-reduced density diagram for CO₂, with areas of near critical liquid and supercritical fluid outlined. This figure illustrates that near the C_p , slight changes in temperature and pressure create large differences in density, causing substantial variations in solvating power. This can also be seen in Figure 2, where large shifts in CO₂ isotherms occur at the C_p of 1070 psi.

It should be noted that although SCCO₂ typically exhibits densities approaching that of liquids, it retains the high diffusivity and low viscosity characteristics of a gas, giving it exceptional penetrating power (Hoyer, 1985). These characteristics may give SCCO₂ an advantage over NCCO₂ for the extraction of oil from water, even though it may be less dense than NCCO₂ at specific temperatures and pressures.

A summarization of the factors that govern species solubility in high density fluids such as near critical and supercritical CO₂ is given by Hoyer (1985):

- * Supercritical fluids have solute loadings approaching liquid solvent loadings as densities approach liquid densities. In many cases, supercritical fluid loadings exceed liquid loadings because the higher temperatures at supercritical conditions result in higher solute vapor pressures.
- * Solubility increases with increasing pressure. A dramatic increase in solubility occurs near the critical point as a result of a large change in solvent density.
- * Solubility may increase, remain constant, or decrease with increasing temperature depending on whether solute vapor pressure or solvent density is the dominant factor. At constant solvent density, solubility increases with increasing temperatures.
- * Solubility increases with increasing solvent density.

Carbon dioxide as a solvent was chosen for this study since it is non-toxic, non-flammable, and is environmentally benign. It acts as an extractant at ambient temperatures, separates well from both water and oils, and is easily obtainable in pure form on a commercial basis. **Table 2** lists the sources of industrial carbon dioxide in the

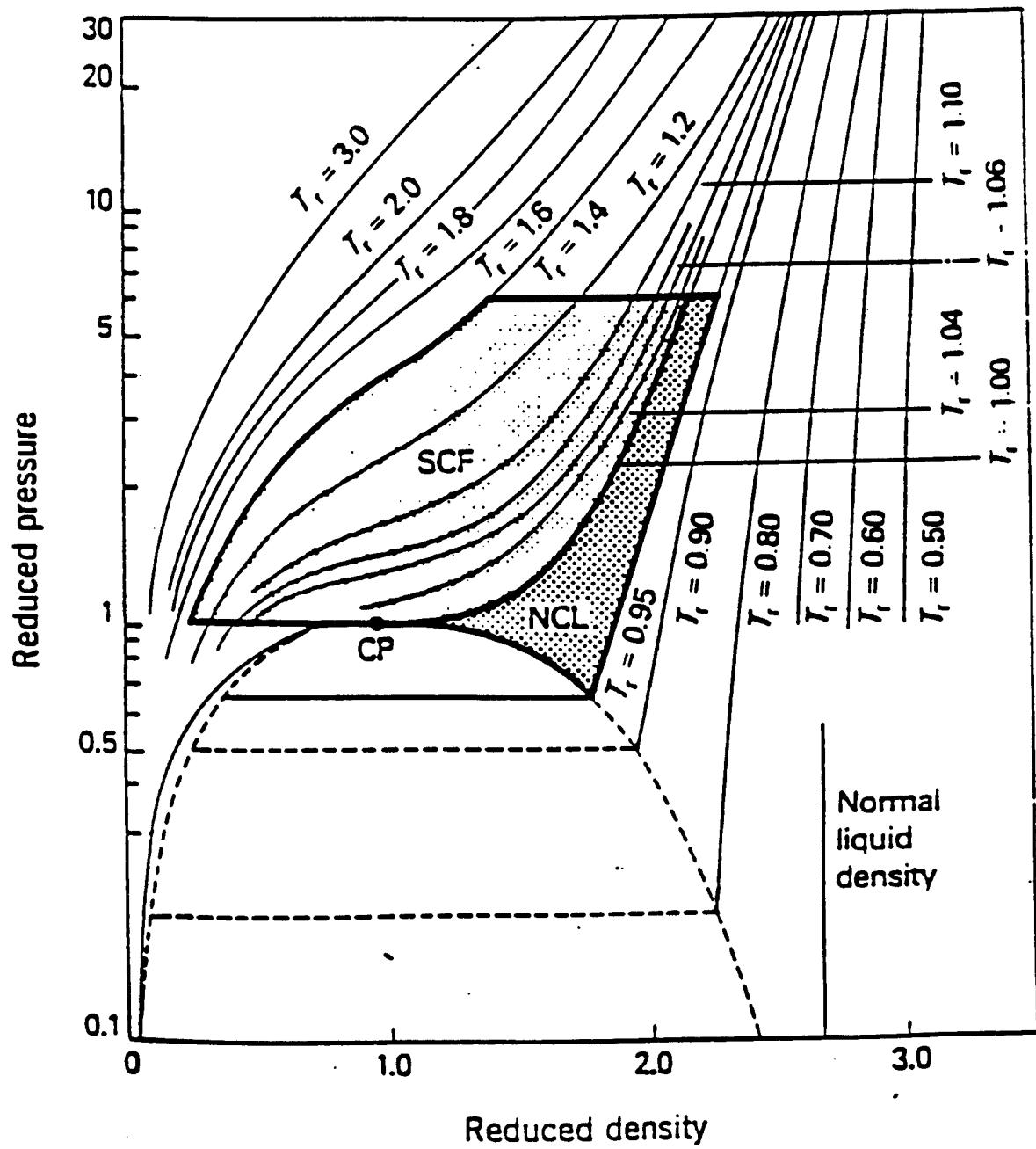


Figure 3: Reduced pressure-reduced density diagram for CO₂.
 Notes: SCF = supercritical fluid, NCL = near critical liquid, CP = critical point, T_r = reduced temperature. Source: Taylor, 1996.

U.S. There is presently a five million ton annual U.S. market for CO₂, while the cost for CO₂ per pound averages \$0.07 to \$0.10 (Carstensen and Pettijohn, 1996).

Table 2: Sources of industrial carbon dioxide.

Source	% Of Total CO ₂ Production
Byproduct of Fertilizer and Chemical Manufacturing	42%
Byproduct of Gasoline Refining	22%
Geological Formations	18%
Byproduct of Ethanol Fermentation	16%
Byproduct of Power/Cogeneration	2%

Source: Carstensen and Pettijohn, 1996

Extraction Process

This study involved a single step process in which emulsified oil in the presence of surfactants was extracted from water by direct contact with near critical or supercritical CO₂. The research incorporated the mixing the oil/water/surfactant emulsion with CO₂ at elevated temperatures and pressures in an extraction vessel for a given time, and then allowing the CO₂ to phase out of solution. In practice, CO₂ containing waste oil would then be transferred to a separator vessel, where isothermal decompression of the CO₂ would take place, causing the oil to fall out of solution. The CO₂ could then be recompressed and used for future extraction, while the oil could be collected, concentrated, and marketed as incineration fuel. **Figure 4** illustrates such a single step, direct contact process; a high pressure counter-flow reactor, with CO₂ entering the bottom of the extraction vessel and flowing against wastewater entering from the top of the vessel.

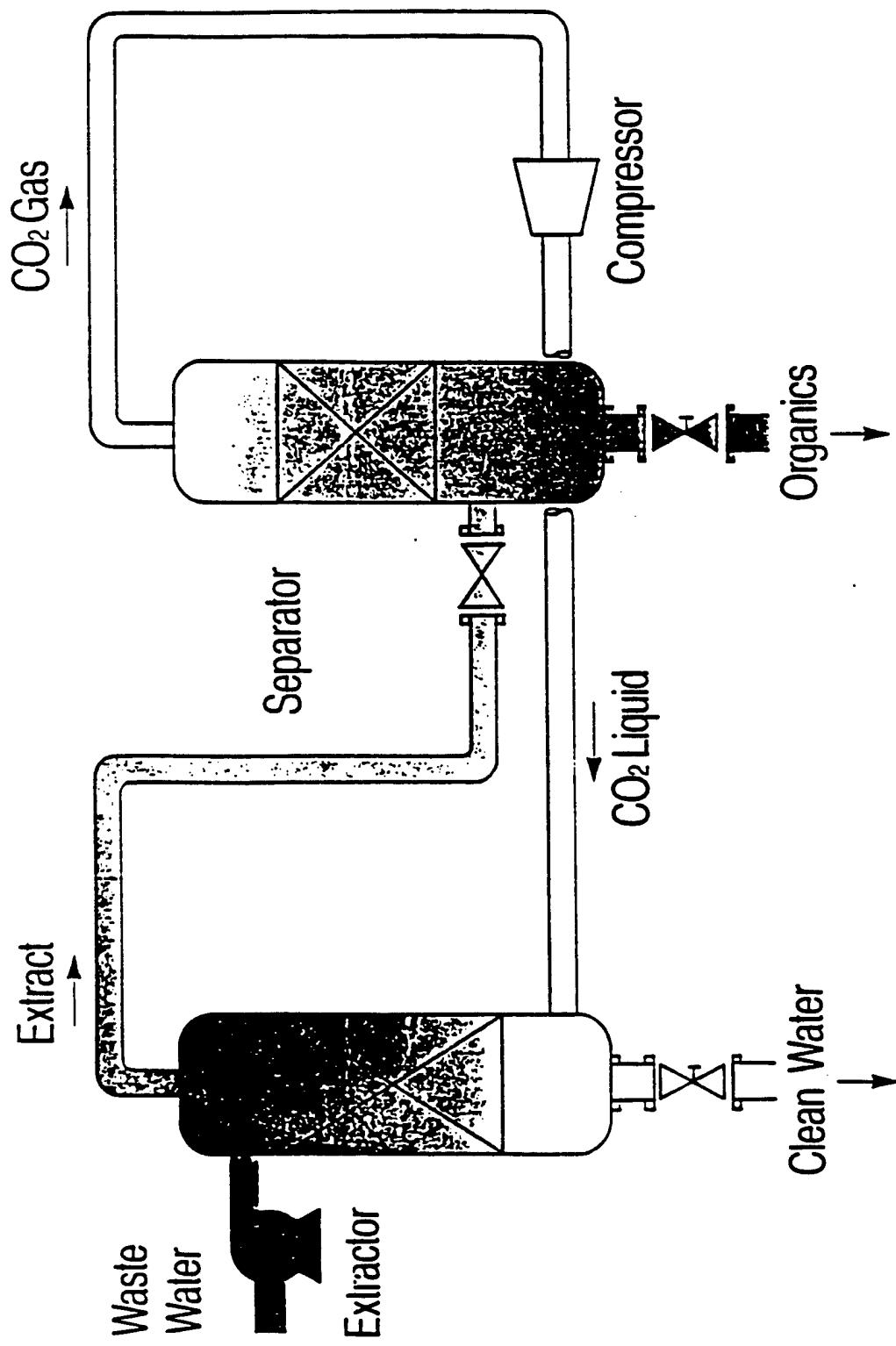


Figure 4: High pressure, counter-flow reactor utilizing single step, direct contact CO_2 extraction of organics from waste water.
Source: CES: *A Breakthrough in Treatment Technology*, 1993.

Chapter 3

LITERATURE REVIEW

Environmental Pollution Control

CO₂ extraction is already a proven process in the beverage and food industry, where it efficiently isolates and concentrates products such as oils, spices, and caffeine. There has been increasing interest in CO₂ extraction in the environmental field. Akgerman et al. (1991) state that three factors contributing to this interest are:

1. The environmental problems associated with common industrial solvents (mostly chlorinated hydrocarbons).
2. The increasing cost of energy intensive separation techniques (for example distillation).
3. The inability of traditional techniques to provide the necessary separations needed for emerging new industries (microelectronics, biotechnology, etc).

To emphasize the attractiveness of CO₂ extraction as an alternative, the authors give the following disadvantages to traditional wastewater treatment processes:

1. Incineration is both energy intensive and requires proper disposal of solid residue (ash).
2. Adsorption requires regeneration of the adsorbent.
3. Biodegradation, although used widely, is slow and necessitates sludge disposal.
4. Liquid extraction (involving liquid hydrocarbons) is a viable technique, but has limited use due to concern over residual solvent present in the processed water.

Wastewater Treatment Studies

An increasing amount of research has been conducted since the early 1980's regarding the applicability of CO₂ extraction to the treatment of wastewater. These studies involved the removal of water-borne organic contaminants by single step, direct contact with CO₂ at elevated temperatures and pressures, and can be divided into the following three categories:

- dynamic systems; counter-flow extraction
- static systems; impeller mixing
- a steady state system

Dynamic Systems: Counter-Flow Extraction

Farncomb and Nauflett (1995) investigated CO₂ extraction of explosives from water. Two tests were conducted at 60°C, with pressures from 3000 to 5000 psi. A 500 mL extraction vessel was used for each test. In the first test, 2052 g of CO₂ was used to extract 200 mL of 1725 mg/L PGDN and 10.7 mg/L 2NDPA in water, which resulted in the complete removal of the explosives. In the second test, 2964 g of CO₂ was used to extract 244 mL of 475 mg/L NG and 6.7 mg/L 2NDPA in water, which resulted in removal of all but 2.1 mg/L of NG. Flow rate of the CO₂ was not given.

Ehntholt et al. (1983) reported on CO₂ extraction of a large number of organic constituents from water, including biphenyls, phthalates, aldehydes, phenols, ketones, chlorodecane, furfural, and caffeine. Concentration of constituents averaged 50 ppb. Two tests were conducted in which 400 mL of sample was extracted by 300 mL of CO₂

over 30 minutes. In the first test, the temperature was 45°C and pressure was 2500 psi, while the second test used a temperature of 30°C and a pressure of 1500 psi. Results ranged from complete removal of methylphenol to only 19% removal of caffeine. Extraction vessel size was not given.

Static Systems: Impeller Mixing

Sako et al. (1995) reported on the extraction of furfural from water using CO₂. Tests were conducted at 30°, 50°, and 70°C at 725.2 psi. Impeller speed, amount of CO₂ used, concentration of furfural, and sample size was not given, though a 500 cm³ extraction vessel was used. Contact time between CO₂ and water varied from 240 to 300 minutes. The authors found that furfural concentrations were highest in the CO₂ at 30°C, and they also calculated the vapor-liquid-liquid-equilibrium (VLLE) of the system at all three temperatures. They then investigated the applicability of the Peng-Robinson equation of state (Peng and Robinson, 1976) combined with the composition dependent mixing rule (Panagiotopoulos and Reid, 1986) and found that it predicted the VLLE of the system with reasonable accuracy.

Akgerman and Carter (1994) investigated the CO₂ extraction of 2,4-dichlorophenol from water. Tests were conducted at 25° and 46°C, at pressures of 1610, 2321, 2408, 2814, and 3321 psi, and a 300 cm³ extraction vessel was used. Contact time between the sample and the CO₂ was 240 minutes. The authors found that the partition coefficient of the dichlorophenol, between water and CO₂ (C_{CO_2}/C_w) increased with increasing

temperature and pressure. The authors also deemed a two hour time period necessary for the phases to separate after the mixing process.

Yeo and Akgerman (1990) reported on the extraction of benzene (0.13 wt. %), toluene (0.05 wt. %), naphthalene (0.0024 wt. %), and parathion (0.0019 wt. %) from water using CO₂. Tests were conducted at 45° and 57°C, within a pressure range of 1131 to 1595 psi, using ternary systems (water + one constituent + CO₂) and a six component system (water + all four constituents + CO₂). Contact time between each sample and the CO₂ was 240 minutes, and a 300 cm³ extraction vessel was used. The authors found that the distribution coefficients (C_{CO₂}/C_w) of all four constituents between water and CO₂ in both the six-component and ternary systems were greatest at 45°C coupled with the highest pressure. The authors also found that the distribution coefficients for each constituent in the six-component system increased compared to those of the ternary system. They also found that the Peng-Robinson equation of state (Peng and Robinson, 1976) used with the composition dependent mixing rule (Pangiotopolous and Reid, 1986) modeled the ternary and six-component systems with reasonable accuracy.

Roop and Akgerman (1989) investigated the effects of co-solvents on the extraction of 6.8% phenol from water by CO₂. Tests were conducted at 25° and 50°C, with pressure at 4003 psi, and a 300 cm³ extraction vessel was used with 150 mL of sample. Contact time between the CO₂ and sample was 180 minutes (one hour contact time, two hour phase separation period). Of nine co-solvents studied (pentane, hexane, octane, 1-pentene, toluene, dichloromethane, chloroform, benzene, and chlorobenzene), benzene was determined to be the most effective co-solvent, increasing the distribution coefficient of

phenol (C_{CO_2}/C_w) up to 50%. The authors also concluded that an effective co-solvent must be soluble in supercritical CO_2 and insoluble in water.

Roop et al. (1988) studied the extraction of 2% creosote from water. Tests were conducted at 25°, 50°, and 75°C, at pressures of 508 to 4003 psi. Sample size was 150 mL, and a 300 cm³ extraction vessel was used. Contact time between CO_2 and sample was 120 minutes (1 hour mix, 1 hour phase out). Using bioassays (rodent embryo cultures) the authors calculated the distribution coefficient of creosote between water and CO_2 (C_{CO_2}/C_w) at the given temperatures and pressures, finding that the highest distribution coefficient for all pressures occurred at 50°C, with coefficients decreasing with decreasing pressure. The authors also state "Appreciable extraction of toxic contaminants (contained in the creosote) was not accomplished until the critical pressure of CO_2 was exceeded."

A Steady State System

Ghonasi et al. (1991) studied the extraction of the following solutions in water using CO_2 ; phenol (7.8%), p-chlorophenol (1.5%), m-cresol (0.3%), and benzene (0.05%). Sample and CO_2 were compressed and then fed together continuously into a high pressure static mixer. After mixing, the solution was transferred to a 30 cm³ separator vessel containing a windowed cell, where phase out occurred. Each phase was then bled off continuously for analysis. Temperature of the static mixer and separator vessel was maintained by a constant temperature water bath. Tests were conducted at 40° and 50°C over a pressure range of 1400 to 2500 psi. The system took 45 minutes to reach steady

state. The authors calculated distribution coefficients for each of the constituents at both temperatures over the pressure range. Over the pressure range, distribution coefficients for phenol, p-chlorophenol, and benzene at 40°C were larger than the coefficients at 50°C. The distribution coefficients for m-cresol varied over the pressure range, but showed definite trends. The authors also used an equation of state described by Carnahan and Starling (1969, 1972) and DeSantis et al. (1976), along with simple van der Waals mixing rules to accurately model their results.

Large Scale Industrial Application

Since 1991, Clean Harbors Environmental Services of Quincy, Massachusetts has operated a 30,000 gallon per day liquid CO₂ extraction facility in Baltimore, Maryland. This facility employs a counter-flow reactor to treat industrial wastewater via a one step, direct contact process of CO₂ extraction (**Fig. 3**). After extraction, the “dirty” CO₂ is transferred to a separator vessel where it is decompressed and the extract is separated. The CO₂ is then recompressed for further extractions.

This method of treatment is able to remediate wastewater with up to 30% organic contamination (*CES: A Breakthrough in Treatment Technology*, 1993). Some of the constituents removed by the liquid CO₂ include (*CES: A Breakthrough in Treatment Technology*, 1993):

- acetone and other ketones
- isopropanol, butanol and higher molecular weight alcohols

- halogenated organics such as carbon tetrachloride, methylene chloride and chlorform
- aromatics, including benzene, toluene, xylene, and ethyl benzene
- acetonitrile and other nitriles

Extraction of wastewater is carried out at 18.3° and 21.1°C in several batch modes per day, and incorporates an extractor vessel ten feet in diameter and three stories in height.

Although SCCO₂ extraction is a relatively new method for the treatment of industrial wastewater, it has been used for some time in the food and beverage industry. McHugh and Krukonis (1994) give the following processes utilizing SCCO₂ extraction:

- decaffeination of green coffee beans
- recovery of edible oils from soybeans, corn, wheat germ, sunflower and safflower seeds, peanuts, and fish
- recovery of essential oils from plants (citrus and limonene oils)

NC/SCCO₂ extraction carried out on the industrial level has typically replaced older methods that used environmentally harmful solvents such as methylene chloride. The primary goal of this technology has always been reduction of environmental pollutants.

Chapter 4

MATERIALS AND METHODS

Materials

Bilge Water Models

Specially prepared models of bilge water were used for this study. Information provided by the USN specified that the bilge water models contain no less than 300 mg/L oil in water and approximately 25 mg/L detergent in water. Two separate models were prepared for each batch test; bilge water containing oil only, and bilge water containing oil and detergent. All samples were prepared from a single oil mix and a single detergent mix supplied by the USN. The oil mix consisted of several light-end machining and lubricating oils, while the detergent mix consisted of several common household detergents, all of which are presently found in Naval bilge water.

Apparatus

Equipment for this study consisted of a bench scale automated extraction system manufactured by Supercritical Fluid Technologies of Newark, Delaware, and an extraction vessel manufactured by Autoclave Engineers, Inc., of Erie, Pa.

Bench Scale Automated Extraction System

The bench scale extraction apparatus consists of a programmable logic controller system which allows for control of the organic modifier and supercritical pumping modules, the extraction module, the collection module, and temperature zones in the extractor, valve ovens, and collection module. This allows for the complete control of extraction time and mode (dynamic or static), extraction pressure, rate of pressurization and depressurization, impeller speed, rate and time of co-solvent addition, and temperature both inside and outside the vessel. The system utilizes a microprocessor for data capture and storage.

Carbon dioxide is supplied to the system via cylinder and compressed by an air driven liquid/gas booster pump, rated to 10500 psi (>700 atm). The pump has a capability of 19 L/min liquid CO₂, is single air head, and operates on a ratio of 115:1. An external chiller on the CO₂ input line eliminates cavitation problems caused by heat of compression at high flow rates. Liquid CO₂ enters the extraction vessel directly from the pump, and post extraction flows through an exit line to a dynamic/static valve, which allows for extraction in dynamic or static mode. Afterwards, the CO₂ flows through a variable restrictor valve, which is heated to prevent clogging by dry ice. This valve is operated manually, allowing for variation in de-pressurization rate. A collection vessel and decompression vent at the end of the line allow for trapping of any extract obtained during the test. A de-pressurization valve located before the dynamic/static valve offers the option of decompressing the vessel quickly, without the benefit of collecting any extract. This valve is also heated to prevent clogging by dry ice. **Figure 5** shows a generalized schematic of the system.

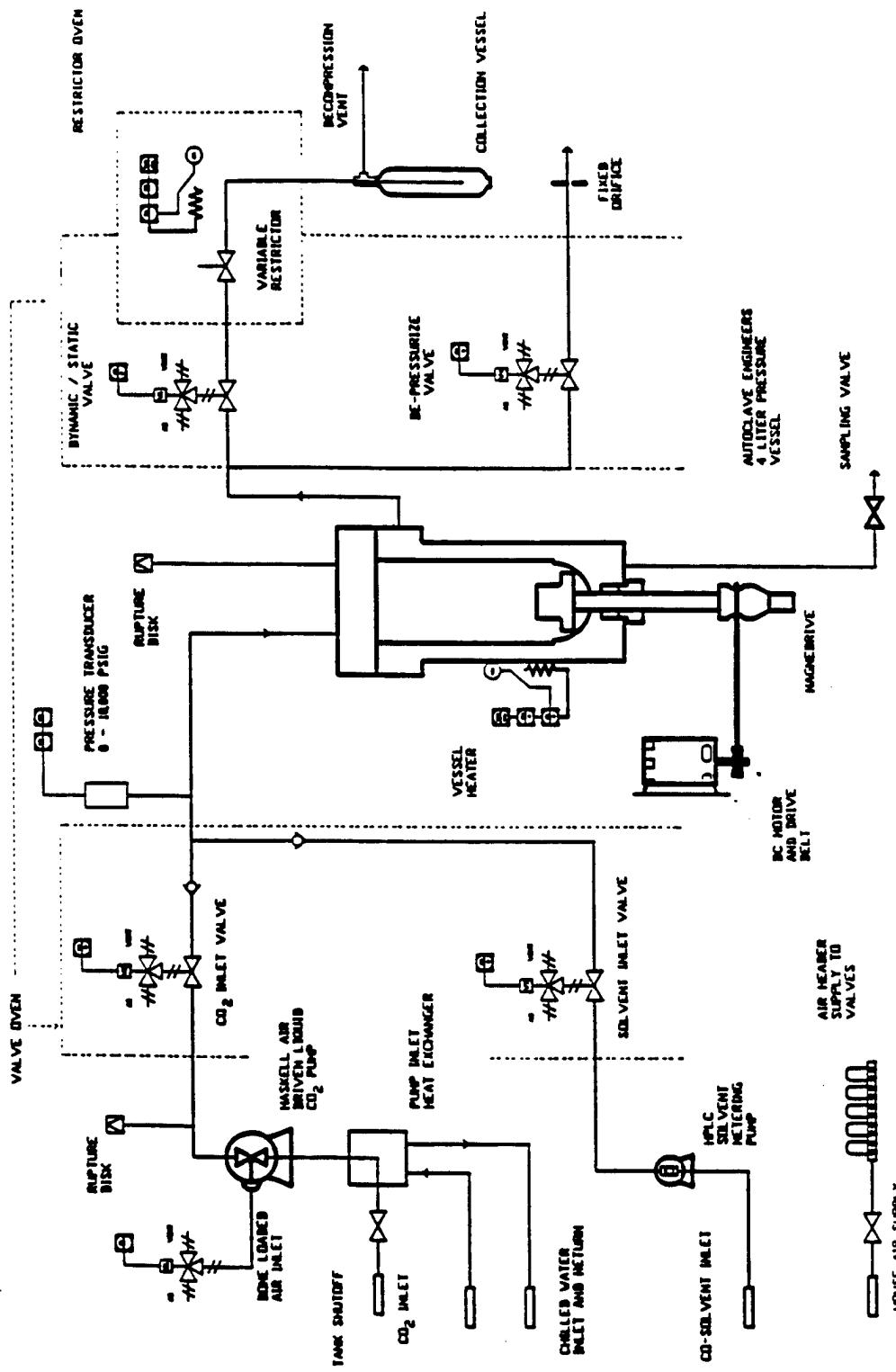


Figure 5: Schematic of bench-scale automated CO₂ extraction system used in this study.

The extraction vessel is a stirred reactor with 4 L capacity. It is constructed of 316 SS, and is rated to 6000 psig (408 atm) at 343°C. It consists of the following: body, cover, closure bolts, seal ring (buna rubber), 7 inlet/outlet ports (3 top, 2 side, 2 bottom), and a magnedrive with lower shaft, coupling, and agitator. The vessel is enclosed in a heating jacket for temperature control. CO₂ is pumped into the vessel through one of the top ports and exits via one of the side ports. A high-pressure shut-off valve (Hoke) was fitted to one of the bottom ports and coupled with a high-pressure micro-metering valve (Hoke) for sample bleed and drain during and after extraction.

The magnedrive is powered by a 2.5 HP industrial motor (Baldor), capable of delivering 60 inch pounds of torque and 2500 RPM. The agitator consists of a six-blade, dual disc, flat turbine impeller (Gaspersator). This system features a hollow lower shaft with a cross drill near the bottom of the cover which draws the CO₂ down the inside of the shaft and out the impeller tips for superior mixing. **Figure 6** shows the extraction vessel assembly.

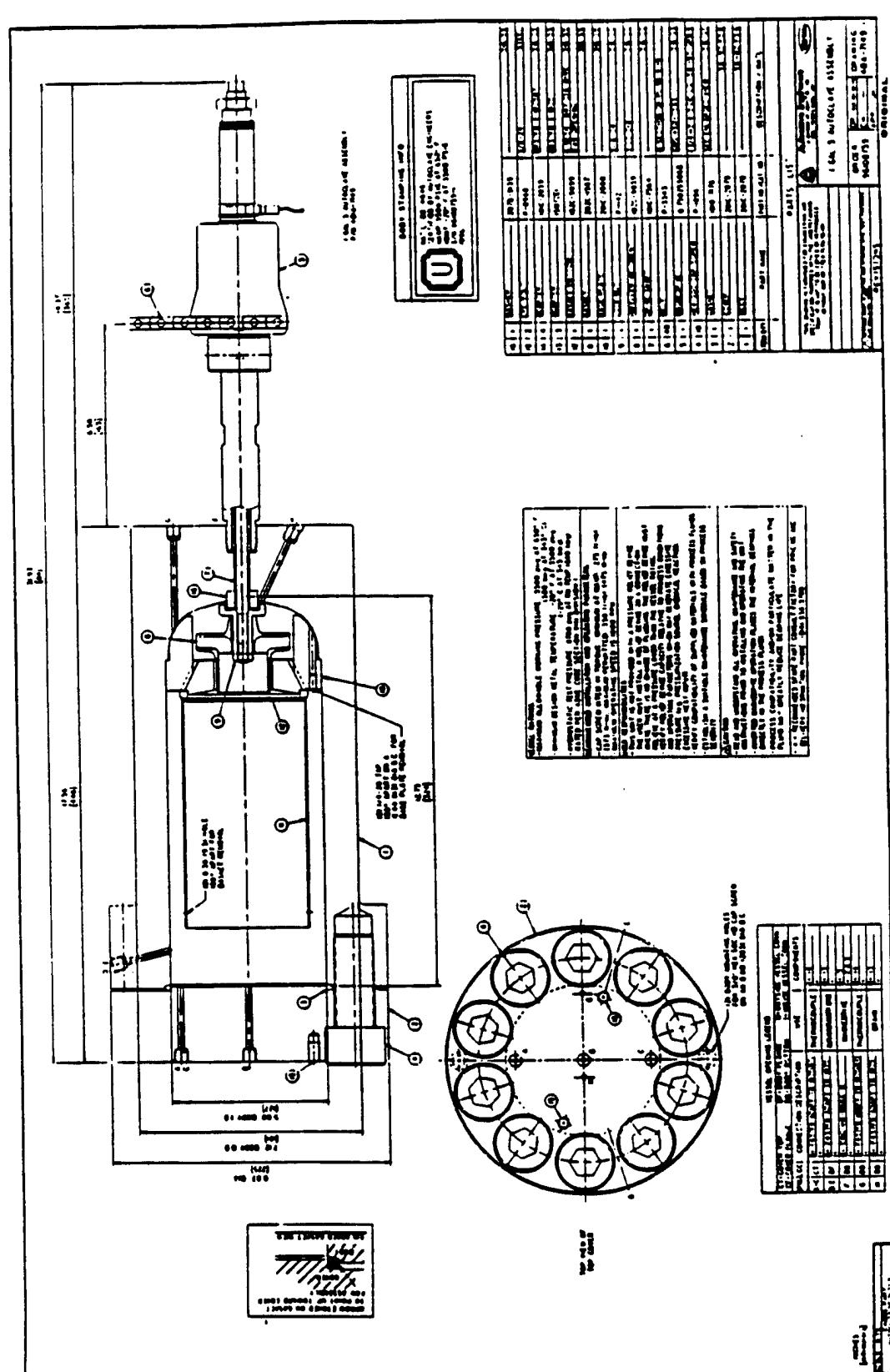


Figure 6: Extraction vessel assembly.

Methods

Analytical Procedure

The analytical procedure used was supplied by the USN, and is very similar to EPA Method 418.1: Total Recoverable Petroleum Hydrocarbons (Spectrophotometric, Infrared). The Naval method consists of solvent extraction followed by infrared spectrophotometer analysis. Dispersed or emulsified mineral oils are extracted from water by intimate contact with Freon 113 (1,1,2-trichlorotrifluoroethane). The solvent extracted fraction is passed through silica gel (70-230 mesh) to reduce any interference due to the presence of materials such as detergents, and then scanned by a Fourier Transform Infrared Spectrometer (FT-IR). Although the method called for a grating IR to be used, it was decided to use an FT-IR because of its superior power and precision. The integrated area under the absorbance peaks between wave numbers 3200 cm^{-1} to 2700 cm^{-1} is used to calculate the concentration of oil in the aqueous sample. These wave numbers represent the carbon-hydrogen stretch present in hydrocarbons.

Since Freon is not a good solvent for heavier oils, and the presence of detergent in oily water causes Freon to form a tight emulsion that makes separation difficult, a calibration curve of oil in Freon using the same oil mix as that in the bilge water samples was run. Using a stock solution of 500 mg/L oil in Freon, standards ranging from 2.7 to 326 mg/L oil in Freon were scanned by an FT-IR (Mattson) located at Research Park. Several spectrograms from the standard curve are shown in **Appendix A**. The number on each spectrogram above and to the left of wave number 2800 is the integrated area under the

peaks, and is used to calculate results from batch testing. Sample preparation for FT-IR analysis is given in **Appendix B**.

Model Bilge Water Preparation

As stated earlier, all models of bilge water were prepared from separate oil and detergent mixes supplied by the USN. The most difficult step of sample preparation involved creating a stable oil in water emulsion. Initially, a hand-held homogenizer was purchased to create the emulsion, i.e. a “raw” sample on which to run CO₂ extractions, but proved difficult and awkward to use. After 45 minutes of homogenizing a 2.2 L volume of water containing 660 mg of oil (300 mg/L), a sizable oil skim was still present on the surface. In addition, more oil was lost as the shaft of the homogenizer became coated with oil, which could not be removed by the homogenizing action. To reduce variability, and also to reduce sample preparation time, the impeller of the extraction vessel was employed in an attempt to create a raw sample. 2.2L of water was placed in the extractor vessel along with oil (measured gravimetrically), and the impeller run for the following time periods at the following RPM’s:

- 306 mg/L oil in water mixed for 30 minutes, impeller speed at 1000 RPM
 - 420 mg/L oil in water mixed for 45 minutes, impeller speed at 1200 RPM
 - 463 mg/L oil in water mixed for 45 minutes, impeller speed at 1200 RPM
 - 461 mg/L oil in water mixed for 45 minutes, impeller speed at 1200 RPM
- note: The vessel was not charged with CO₂ during the tests.

The maximum impeller speed at which excessive vibration of the extraction equipment does not occur is 1200 RPM. After the mixing period (raw mix period), the

impeller was turned off, and a sample was taken from the bottom of the extraction vessel every 0.5 hr for 2 hr. Between each test, the vessel was cleaned manually with acetone and clean rags, then rinsed down with D.I. water. A 2 hr time period was chosen to allow adequate time for CO₂ extraction and phase out to take place, i.e. an emulsion (raw sample) is created and then batch testing conducted. A 2 hour time period was also chosen based on the author's own experience performing liquid CO₂ extractions at a previous place of employment. Since batch testing incorporates a 45 minute extraction period followed by a 30 minute period to allow the CO₂ to phase out of solution (again, based on the author's own experience), raffinate (cleaned bilge) samples are taken 1.25 hours after the creation of the raw sample.

Figure 7 shows graphical results of the 4 tests, with exponential trend lines for each. The data indicates a gradual decrease in oil concentration over time. This was verified by visual confirmation of a slight skim of oil seen on the surface of the samples after the tests were conducted and the vessel was being dismantled for cleaning. Results of the first two tests suggested a need for approximately 160 mg/L oil in excess of the initial 300 mg/L oil initial concentration, hence the 460 mg/L oil initial concentration of the following two tests. It was deemed that a 460 mg/L initial concentration, and a raw mix time period of 45 minutes will result in an oil/water emulsion of approximately 300 mg/L 1.25 hours after the emulsion is created. Therefore, if raffinate samples contain less than 5 mg/L oil, than approximately 300 mg/L oil have been removed. However, if 5 mg/L or more oil is present in raffinate, than batch test conditions are not optimal. Note: the 463 mg/L initial C. test may not be representative of the trend (an error may have occurred during the test).

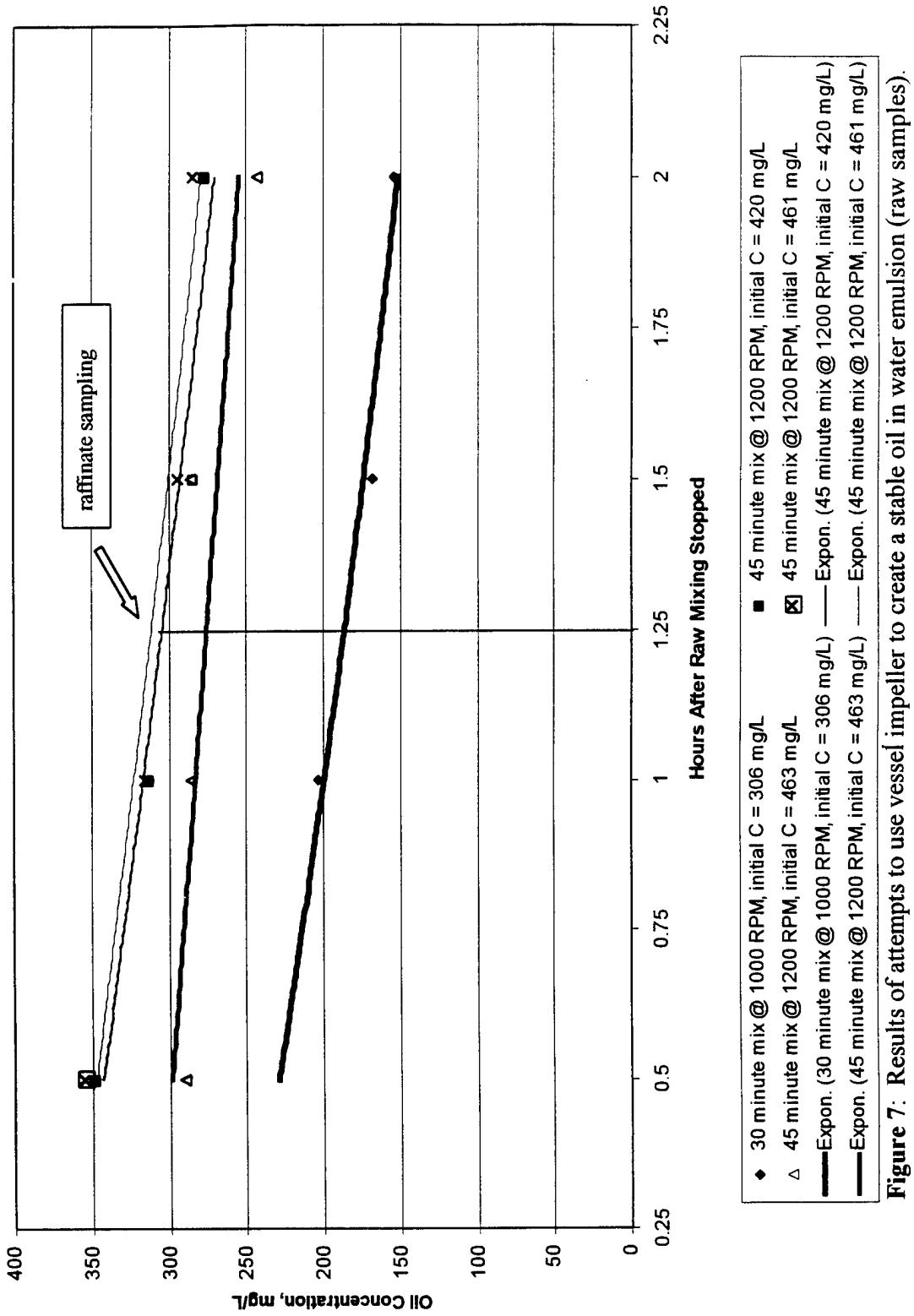


Figure 7: Results of attempts to use vessel impeller to create a stable oil in water emulsion (raw samples).

A fifth test, one that simulated an actual batch test run, but without CO₂ extraction, was also conducted. For this test, 470 mg/L oil in water was mixed for 45 minutes at 1200 RPM (raw mix period), then mixed for 45 minutes at 800 RPM (contact time). Finally, the impeller was turned off, and the sample was allowed to settle for ½ hr (time period allowed for CO₂ phase out).

Figure 8 shows graphical results of this test, which indicate that spinning the impeller at 800 RPM during contact time may actually help to break the emulsion created by the raw mix period. A slower mixing speed may cause small drops of oil in the emulsion to coagulate, increasing the rate at which the oil phases out of solution. However, oil concentration at 1.25 hr after raw mix (again, the point at which raffinate samples are taken) was still 288 mg/L, close to the 300 mg/L concentration stipulated by the USN. **Figure 9** shows a combination of **Figures 7** and **8**.

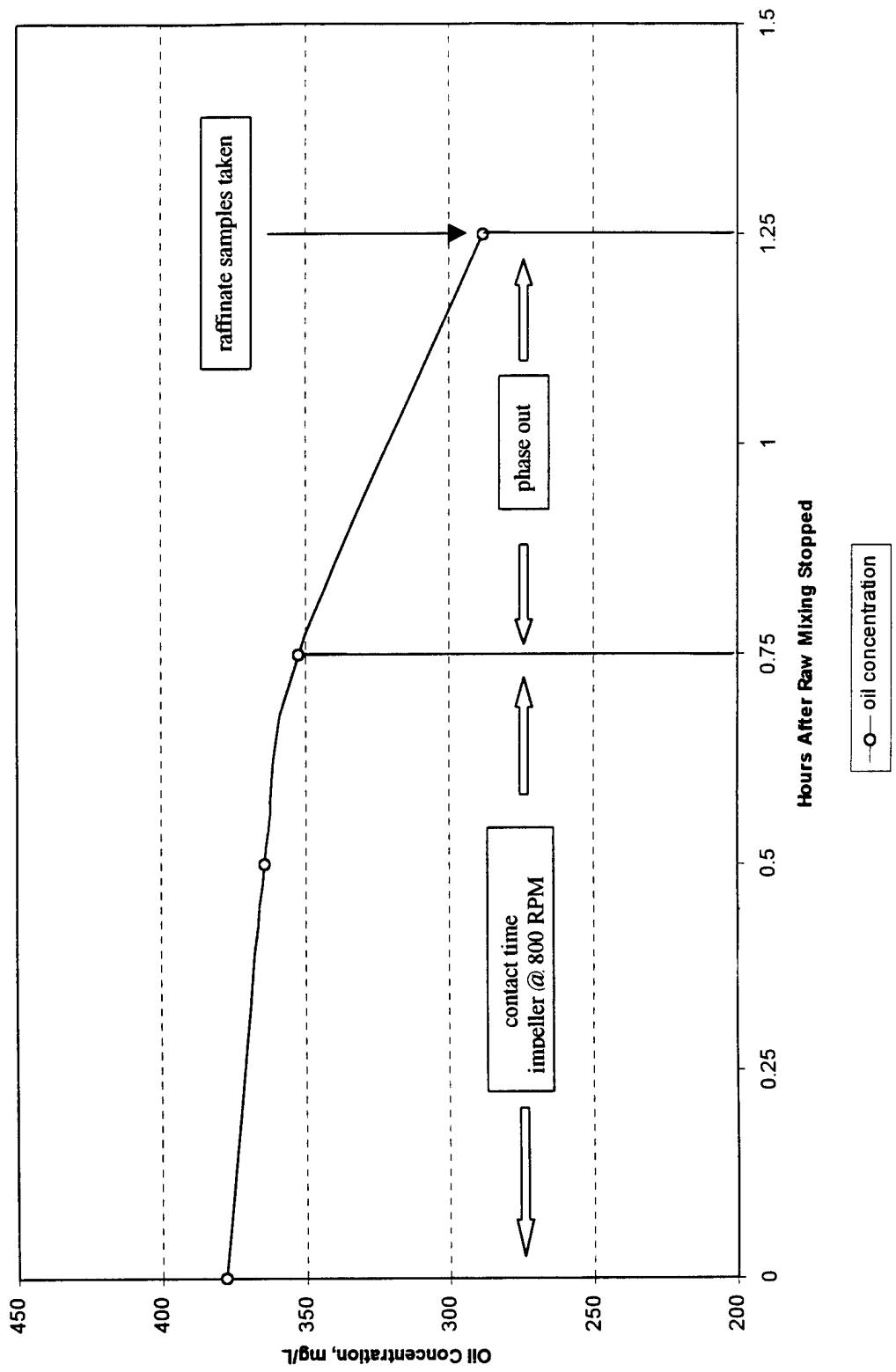


Figure 8: Oil concentration over a batch test simulation (impeller speed = 800 RPM, no CO₂ used).

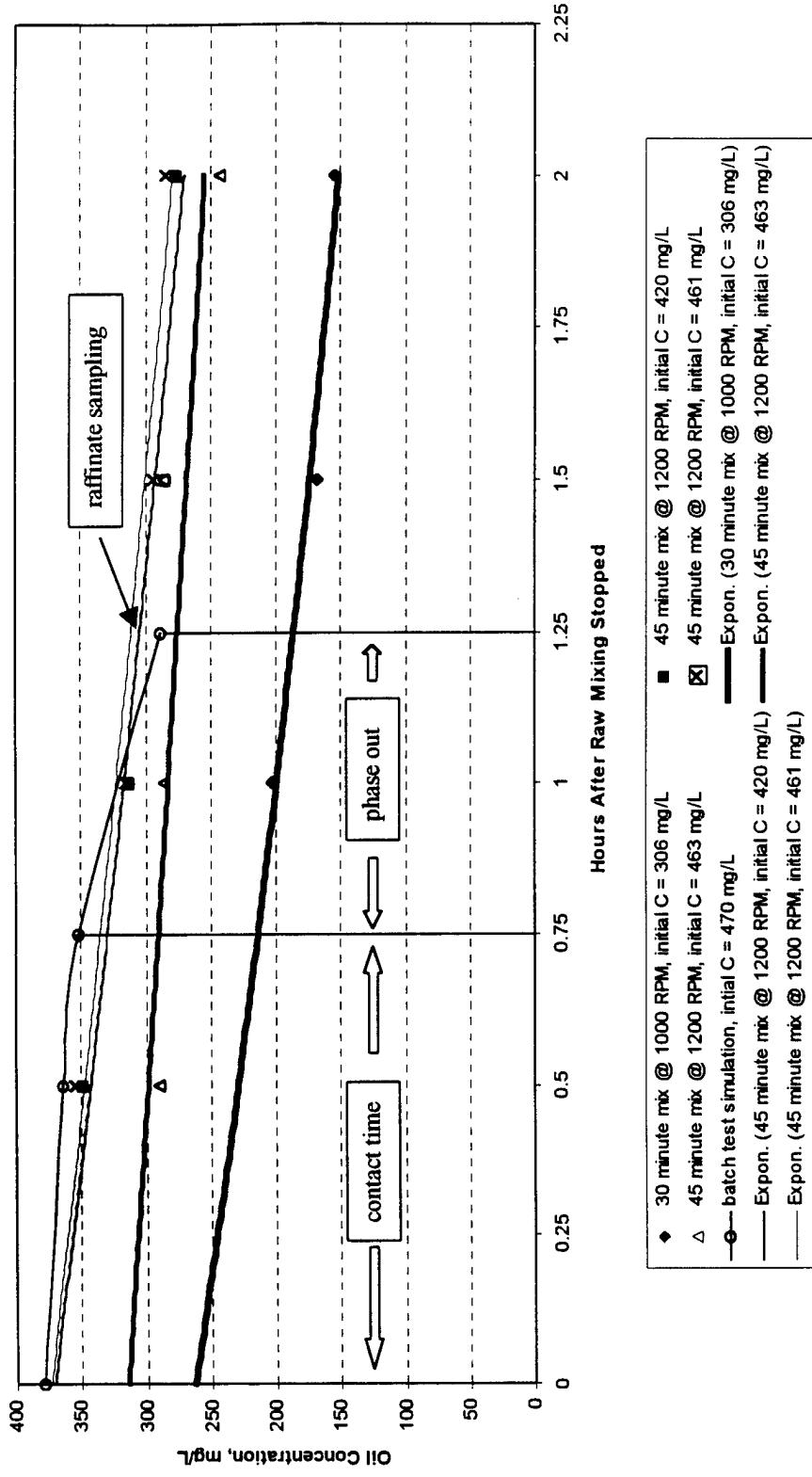


Figure 9: Comparison of oil concentration over a simulated batch test run (no CO_2 used) and oil concentration after the raw mixing period.

Batch Testing Procedure

Initially, the extraction vessel was loaded with 2000 mL of de-ionized water. An additional 200 mL of de-ionized water was then added to the vessel via graduated cylinder. Approximately 1018 mg of oil was then measured gravimetrically and added to the vessel. If a detergent batch test was being conducted, approximately 55 mg of detergent was measured gravimetrically and also added to the vessel. The vessel was then loaded into the extraction apparatus.

Vessel temperature and raw mix impeller speed (1200 RPM) were then programmed, and the impeller and heating process both started. After the raw mix period, the impeller was shut off, the bottom valve line drained (20mL), and a 200 mL sample (the raw sample) was taken by graduated cylinder from a bottom port of the vessel.

Vessel pressure was then programmed and recording of data started. The vessel was then charged with CO₂ in dynamic mode to eliminate air headspace. After reaching pressure, contact time impeller speed (800 RPM) and static mode were programmed, and the extraction begun.

After the desired contact time, the impeller was shut off for CO₂ phase out. After ½ hour, the bottom valve line was again drained (20mL), and 200 mL of sample (raffinate) was taken by graduated cylinder. Recording of data was then stopped, heating discontinued, and the vessel depressurized.

Experimental Matrix and Calculations

The following experimental matrix was used for extractions:

Batch Group	V_w (L)	V_{CO_2} (L)	T		Pressure		Impeller Speed (rpm) RM CT	Contact Time (min)
			°C	°F	Atm	Psia		
Group 1: Near critical CO_2 .	1.98	0.9231	24	75.2	54.5	900	1200 800	45
					68.1	1000		
					81.8	1200		
Group 2: Supercritical CO_2 , 32°C.	1.98	0.9231	32	89.6	74.9	1100	1200 800	45
					88.6	1300		
					102.2	1500		
Group 3: Supercritical CO_2 , 40°C.	1.98	0.9231	40	104	74.9	1100	1200 800	45
					88.6	1300		
					102.2	1500		

note: V_w = sample volume, RM = raw mix, CT = contact time.

Twenty-six extractions were completed at temperatures and pressures matching those in the matrix as closely as possible. After concentrations of raw and raffinate for each test were determined, the partition coefficients of the oil between CO_2 and water were then calculated using the formula

$$K_{CO_2} = \{(V_w/V_{CO_2}) * (C_i - C_f)\}/C_f$$

which was derived as follows:

$$MASS_{Total} = C_{i,H2O} * V_w \quad (\text{oil in water pre-extraction})$$

$$MASS_{H2O} = C_{f,H2O} * V_w \quad (\text{oil in water post-extraction})$$

$$MASS_{CO_2} = V_w * (C_{i,H2O} - C_{f,H2O}) \quad (\text{oil in } CO_2 \text{ post extraction})$$

$$\text{where } C_{CO_2} = V_w * (C_{i,H2O} - C_{f,H2O}) / V_{CO_2}$$

$$\text{therefore } K_{CO_2} = C_{CO_2} / C_{f,H2O}$$

$$= \{(V_w/V_{CO_2}) * (C_i - C_f)\}/C_f$$

The following values were used to calculate K_{CO_2} :

$$V_t = 2.9031 \text{ L} \quad (\text{measured volume of the extraction vessel})$$

$$V_w = 1.98 \text{ L} \quad (\text{sample size} = 2 \text{ L} - 20 \text{ mL for valve drain out})$$

$$V_{CO_2} = 0.9231 \text{ L} \quad (V_t - V_w)$$

$$C_i = \text{concentration of oil in raw sample (mg/L)}$$

$$C_f = \text{concentration of oil in raffinate (mg/L)}$$

It should be noted that neither $MASS_{CO_2}$ nor C_{CO_2} were measured in this study. All K_{CO_2} values were calculated using concentrations of oil in raw and raffinate samples. Therefore, the K_{CO_2} values obtained in this study may best be referred to as apparent K_{CO_2} values, since a mass balance on the oil cannot be performed.

For sample calculations for K_{CO_2} values, please see **Appendix C**.

For an error analysis of batch testing and analytical procedures, please see **Appendix D**.

Chapter 5

RESULTS AND DISCUSSION

Table 3 gives batch testing results. Initially, detergent and non-detergent tests were conducted at three different pressures for each of the temperatures given in the experimental matrix (T setpoint). Concentrations for raw and raffinate samples are Raw C and Raff C respectively. K_{CO_2} was then calculated using initial C and raw C values ($K_{CO_2} I$ and $K_{CO_2} R$ respectively). After K_{CO_2} was calculated for each batch test, duplicate tests were run at pressures at which K_{CO_2} was highest for each batch group.

For all tests except runs 7, 8, 9, and 12, temperature was recorded every 5 seconds for each test (start of pressurization through sampling of raffinate), and a mean temperature was then computed (T Actual). An average temperature was then calculated for each batch group (T Average). Pressure was also recorded every 5 seconds for each test, and an average pressure then computed for each test (P psi). However, for runs 7, 8, 9, and 12, no computer data was collected, so temperature was taken as the setpoint T, and pressure taken as an average of lowest and highest pressures observed during the test.

Oil and Water Models

Figure 10 shows graphical representation of the results for non-detergent tests with K_{CO_2} calculated using raw concentrations. Also included in the graph are best fit lines, polynomial regression trend lines for K_{CO_2} values in each batch group. Group 1 batch

Table 3: Batch testing results. (*no computer data, •V_w = 1.78 L, •V_{CO₂} = 1.1231 L)

Batch Group	Run #	T °C Setpoint	T °C Actual	T °C Avg.	P (psi)	Initial C. mg/L	Raw C. mg/L	Raff C. mg/L	Deterg. C. mg/L	K _{CO₂} I	K _{CO₂} R
1	27	26	890	469	375	6.08				16.3	1.30
	*7	24	900	464	363	2.53				39.1	30.6
	35	24	913	477	369	9.92	0			10.1	.78
	*8	24	1000	465	363	3.45				28.7	22.4
	*9	24	1200	467	346	7.31				13.5	.99
	11	33	1123	464	371	13				74	.59
2	*12	32	33	1300	456	431	20.2	0		34	.32
	15	34	1455	473	390	6.71				14.9	1.23
	•28	34	1466	505	442	4.66				23.0	20.1
	34	40	1129	459	340	7.12				13.6	1.00
	29	40	1153	465	375	12.4				78	.63
	18	40	39	1229	450	364	4.17	0		22.9	.185
3	16	39	1272	471	363	4.4				22.7	1.75
	19	39	1479	460	381	4.88				20.0	1.65
	14	26	896	469	409	191				3.12	2.45
	1	25	24	1028	461	379	195	27		2.93	2.02
	26	28	1189	469	423	158	22			4.22	3.60
	30	28	1192	461	401	158	21			4.11	3.30
2	21	33	1092	477	404	209	28			2.75	2.00
	31	32	34	1278	465	416	174	24		3.59	2.98
	20	33		1294	467	380	148	21		4.62	3.36
	22	34		1485	462	380	170	21		3.68	2.65
	23	39		1185	467	396	232	28		2.17	1.52
	32	40	40	1279	460	382	171	23		3.63	2.65
3	24	39		1288	459	413	187	22		3.12	2.59
	17	40		1484	464	354	199	29		2.86	1.67

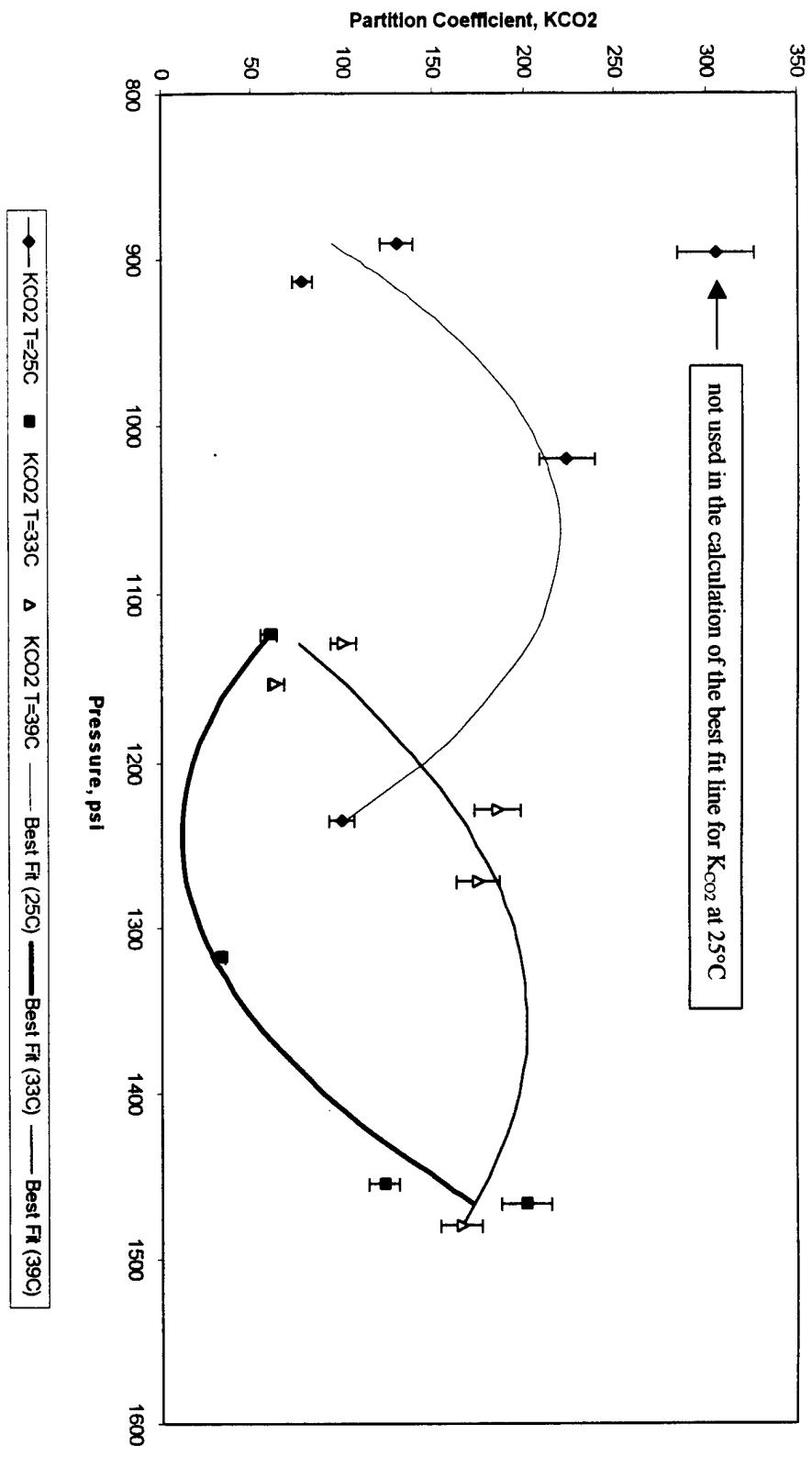


Figure 10: Partition coefficient, K_{CO_2} (raw values used), of the oil mix between water and CO_2 vs. pressure for non-detergent tests.
 note: Error bars are 6.9% of the K_{CO_2} value, determined by an error analysis done on batch testing and analytical procedure
 (Appendix D), and not through multiple experiments.

tests (25°C) contain an outlier (run 7) which was not included in the calculation of the best fit line for that batch group. All best fit lines exhibit curvature, convex for 25° and 39° C , concave for 33°C . This may be the effect of the pressure variation on the solvating power, viscosity, and diffusivity of the CO_2 , as discussed in Chapter 2. Several studies have shown that solvating power of CO_2 may be highest at intermediate temperatures or pressures for various contaminants (Ghonasi et al. 1991, Roop et al. 1988).

Oil, Water, and Detergent Models

Figure 11 shows graphical representation of the results of the detergent tests, with K_{CO_2} calculated using raw concentrations. Curvature in the best fit lines may possibly be caused by the effects of pressure variation on the detergent present in solution as well as on the solvating power of the CO_2 . Critical micelle concentration (CMC) is defined as the minimum amount of detergent necessary in solution to form aggregates. The smallest type of aggregates that are formed are referred to as micelles, defined as organized clusters of surfactant. If CMC has been reached in an oil-water-detergent solution, oil remains in a stable microemulsion because it is held within these surfactant micelles. Beckman et al. (1991) state that “The chemical environment, or polarity, within (a surfactant) micelle...can be varied over a wide range via pressure tuning.” This variation in polarity would affect the ionic interactions of the surfactant head groups, and would in turn influence the ability of the CO_2 to extract the oil from the micelle.

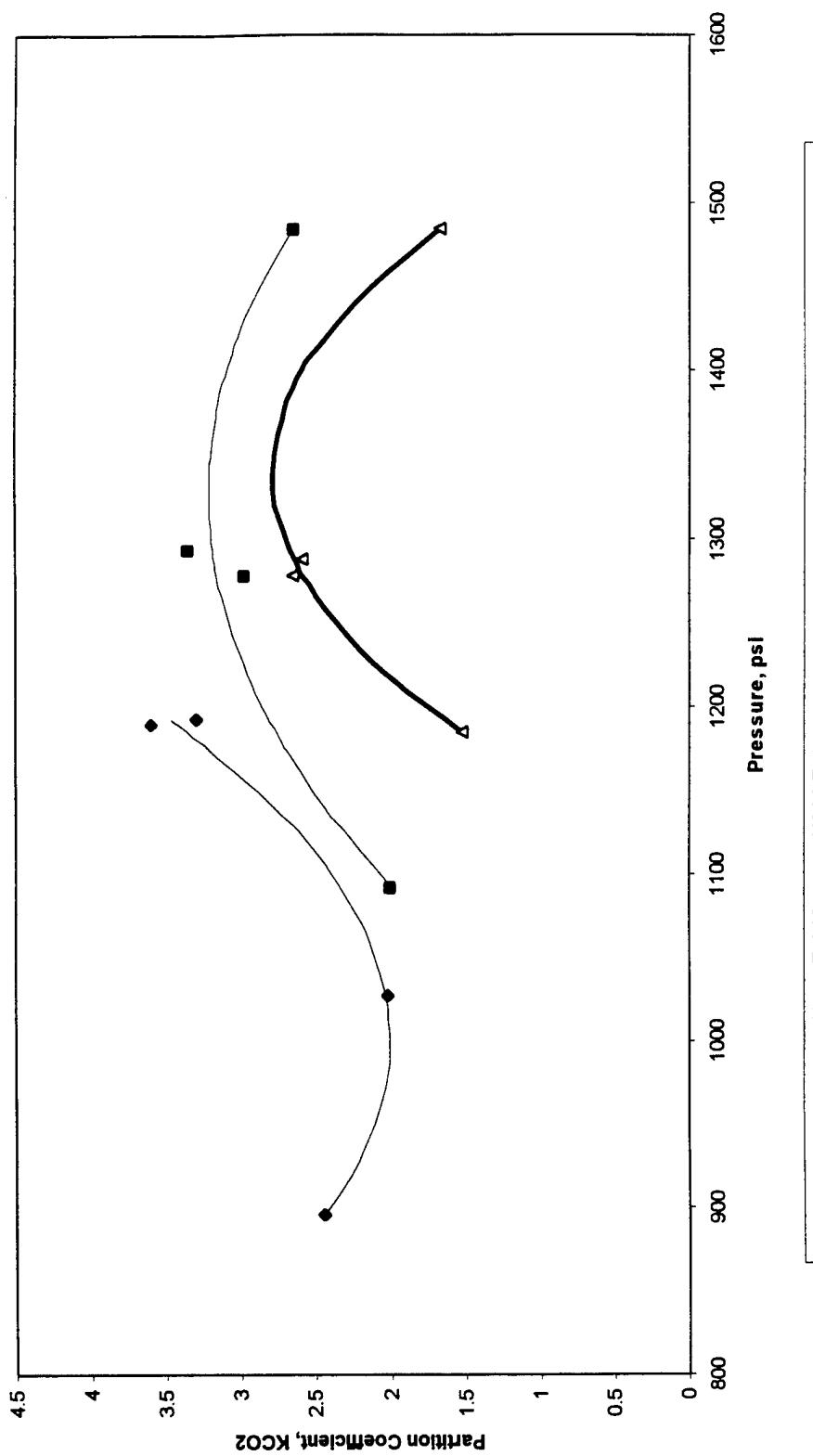


Figure 11: Partition coefficient, K_{CO_2} (raw values used), of the oil mix between water and CO_2 vs. pressure for detergent tests.
note: Error bars are 6.9% of the K_{CO_2} value, determined by an error analysis done on batch testing and analytical procedure (Appendix D), and not through multiple experiments.

Partition coefficients for the detergent tests are on average two orders of magnitude lower than partition coefficients for non-detergent tests. The mixture supplied by the USN contained several different surfactants. Ionic and nonionic surfactants react differently to NC/SCCO₂ under pressure, with solvation of the hydrocarbon tail of the micelle occurring in ionic surfactant systems, while headgroup spacing of the micelle may be affected in nonionic surfactant systems (Beckman et al. 1991). A mixture of detergents containing both ionic and nonionic surfactants could therefore affect the solvating power of NC/SCCO₂ by a large degree.

Comparison of Best Fit Lines
Calculated Using Initial and Raw Concentrations

Figure 12 shows best fit lines for K_{CO₂} values that have been calculated using both initial and raw concentrations from non-detergent tests. These lines parallel one another closely, with best fit lines being greater for K_{CO₂} values calculated using initial concentrations. This is to be expected, since raw concentrations were on average 17% lower than initial mix concentrations. **Figure 13** shows best fit lines for K_{CO₂} values calculated using initial and raw concentrations for detergent tests. These predicted values also parallel one another closely, as in Figure 12.

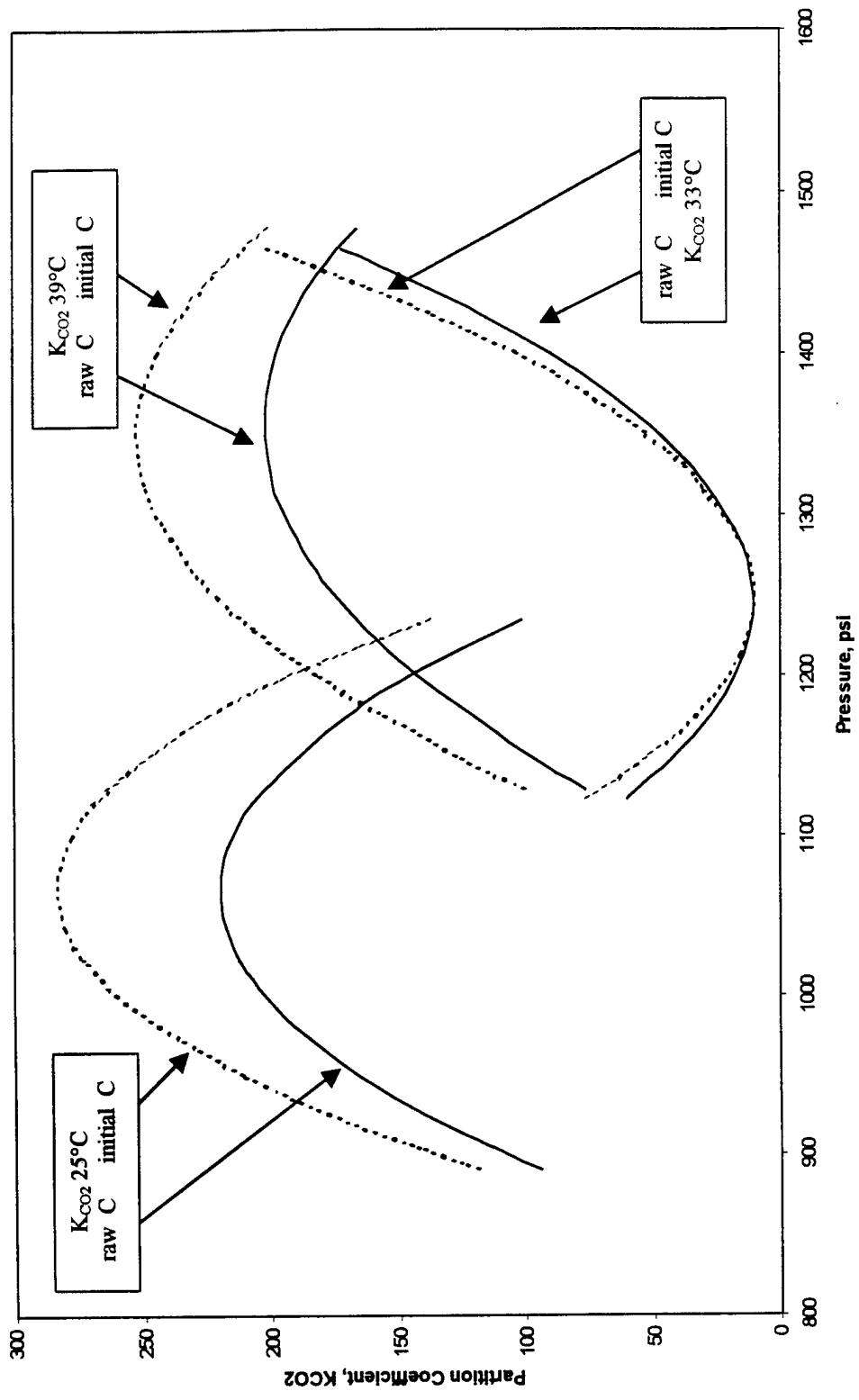


Figure 12: Best fit lines for K_{CO_2} values calculated using initial and raw concentrations of oil vs. pressure for non-detergent tests.

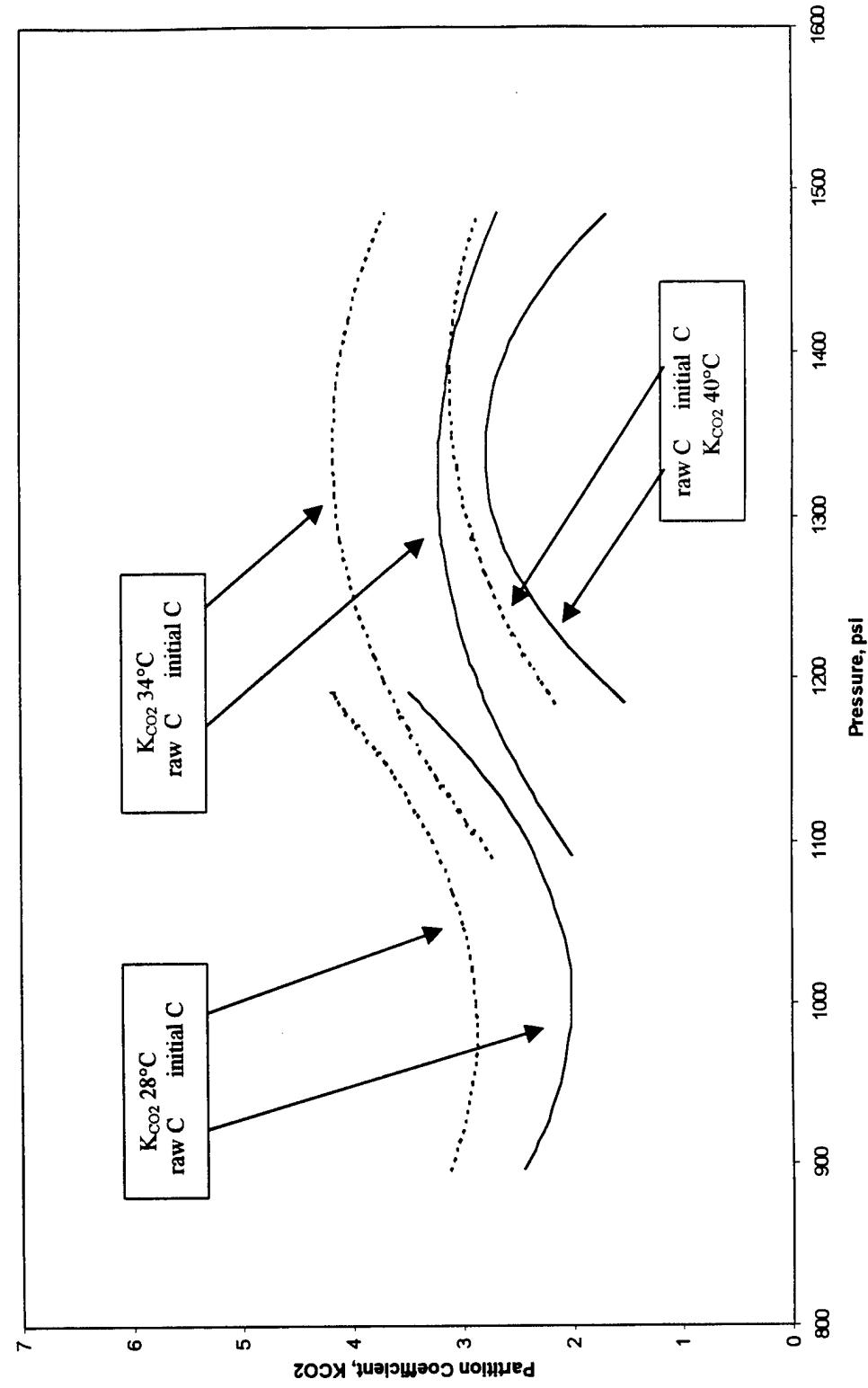


Figure 13: Best fit lines for K_{CO_2} values calculated using initial and raw concentrations of oil vs. pressure for detergent tests.

Factors Affecting Oil Concentration

Factors that could affect oil concentration in raw and raffinate samples include the following:

- * raw mix impeller efficiency
- * effect of detergent on raw mix impeller efficiency
- * differences in the rate of CO₂ phase out between detergent and non detergent tests
- * temperature
- * variations in the amount of detergent added for each detergent test

Figure 14 shows raw mix impeller efficiency, defined as

$$(\text{raw concentration} \div \text{initial concentration}) \times 100.$$

The average raw mix concentration for non-detergent tests was 468 mg/L, while the average for detergent tests was 465m mg/L. The addition of detergent may have enhanced emulsion stability, since the average raw concentration for detergent tests was 395 mg/L, while the average raw concentration for non-detergent tests was 377 mg/L. Impeller efficiency seemed to remain reasonably constant for all tests, since linear regressions for both series of data run closely parallel to one another, each increasing slightly with increased raw mix concentration. Overall raw mix impeller efficiency for non-detergent tests was 81%, for detergent tests, 85%. (note: The outlier at 505 mg/L is the result of run #28, in which an incorrect V_w was accidentally used.)

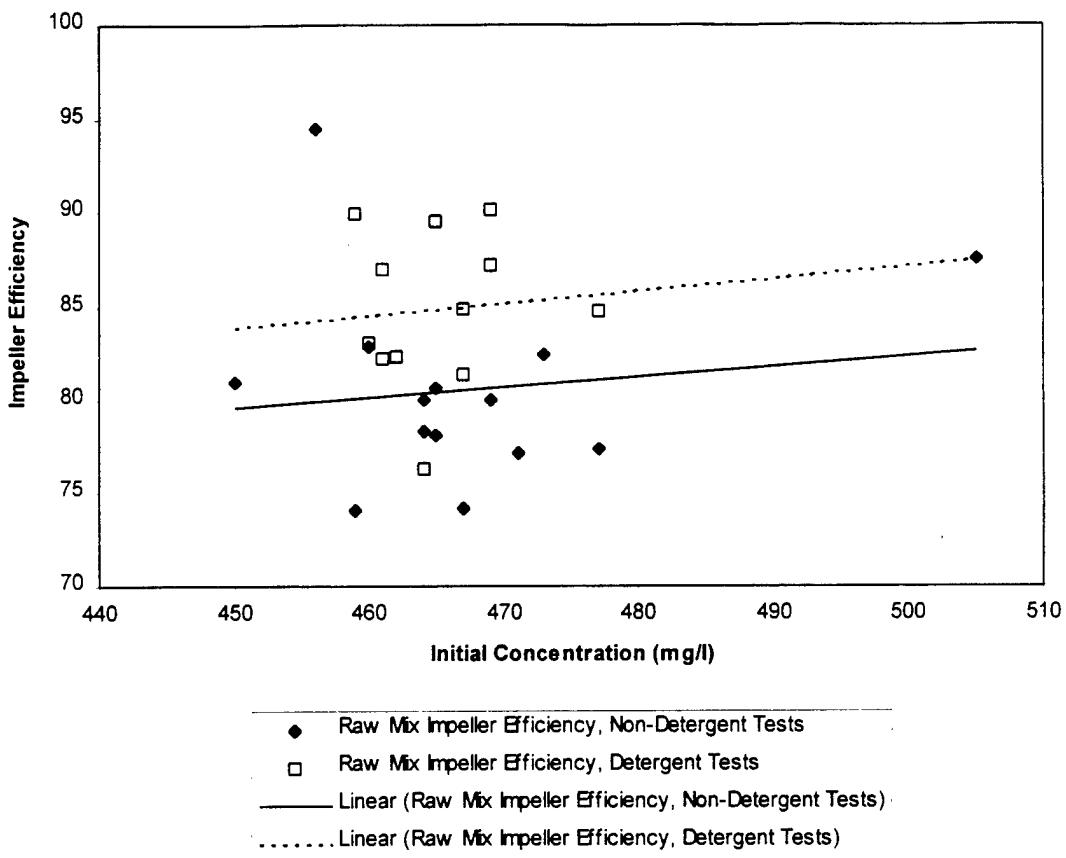


Figure 14: Raw mix impeller efficiency vs. initial concentration.

Figure 15 shows partition coefficients over time for a typical detergent batch test (run #14, 26°C, 896 psi, 23 mg/l detergent). Results indicate that the partition coefficient, K_{CO_2} , increases only slightly throughout a 13 hour time period after the raffinate sampling. This would seem to verify that the addition of detergent acts to create a stable oil/water emulsion after extraction by CO_2 , and that K_{CO_2} values would not be significantly higher for detergent tests if a longer phasing out period had been used in the study. For non-detergent tests, similar data was not collected, and future research may need to be conducted in this area.

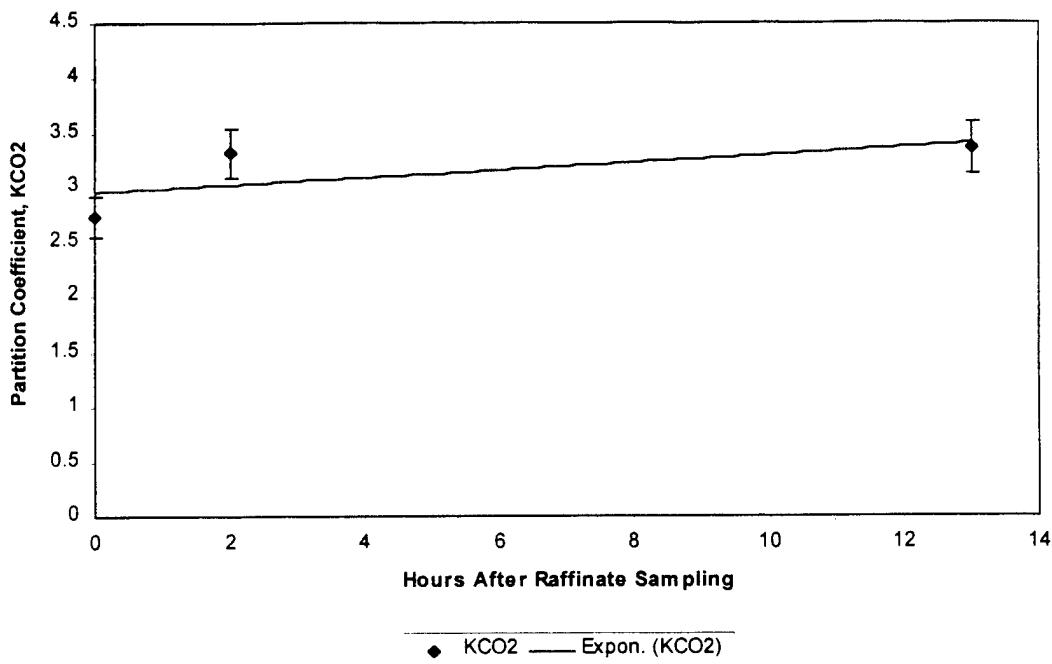


Figure 15: Partition coefficient, K_{CO_2} , of the oil mix between water and carbon dioxide vs. hours after raffinate sampling for a typical detergent test, run #14.

Figure 16 shows raw mix impeller efficiency vs. temperature for all tests (excluding those with no computer data) with a linear regression trendline. The data indicates that overall impeller efficiency remained reasonably constant throughout the temperature range. **Figure 17** shows raw mix impeller efficiency vs. concentration of detergent with a linear regression trendline. Data indicates that impeller efficiency was not greatly affected by variation of detergent concentration in the range of 21 mg/L to 29 mg/L.

Figures 14, 16, and 17 show that despite addition of detergent and variation in temperature and amount of detergent added, impeller efficiency remained reasonably constant throughout the study, at approximately 83%. Figure 15 shows that K_{CO_2} values for a detergent test increase only slightly over a 13 hr time period after raffinate sampling, demonstrating that oil not extracted from solution by CO_2 remains in a stable emulsion.

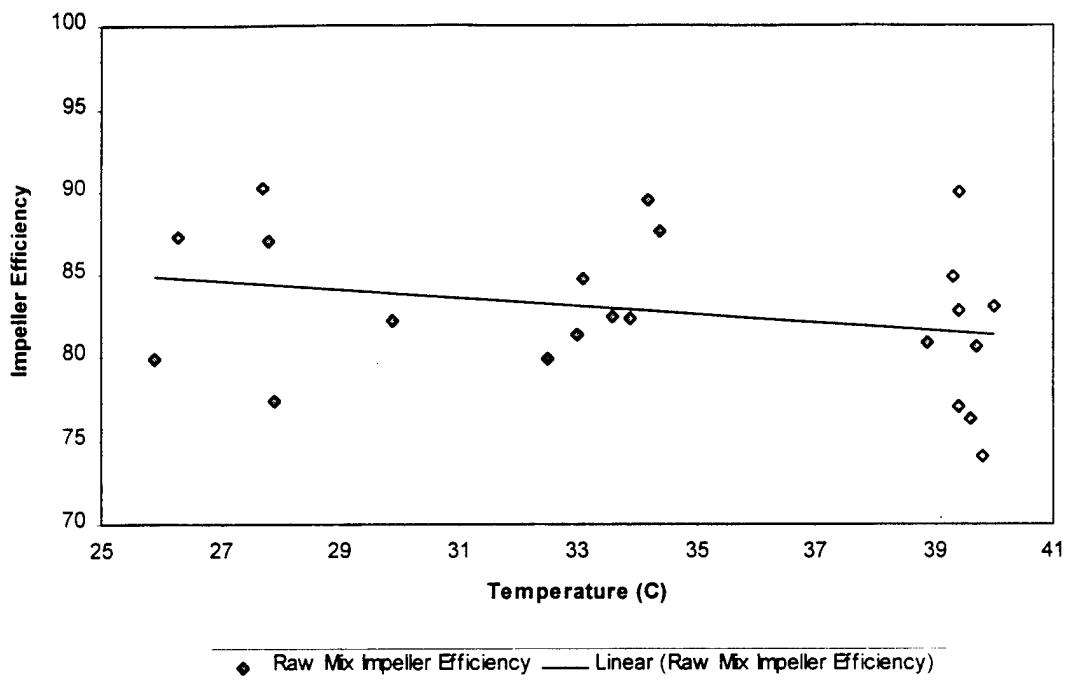


Figure 16: Raw mix impeller efficiency vs. temperature (all tests)

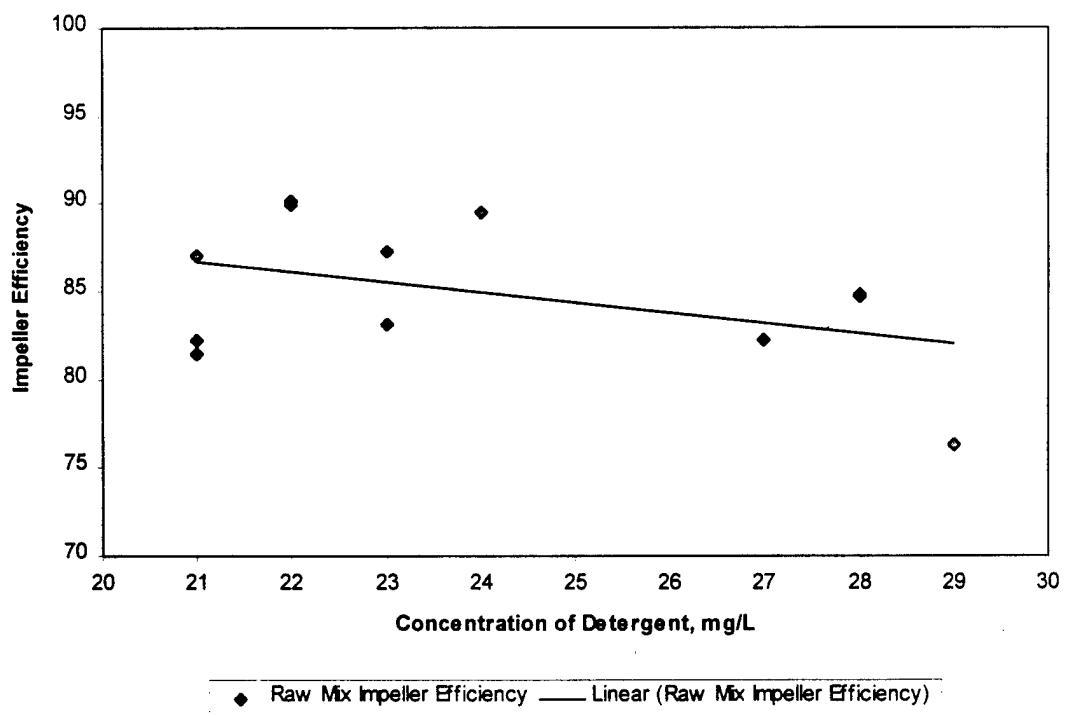


Figure 17: Raw mix impeller efficiency vs. concentration of detergent.

Chapter 6

CONCLUSIONS AND RECOMMENDATIONS

This proof of concept study shows that NC/SCCO₂ extraction of oil from bilge water models is affected greatly by the addition of detergent. K_{CO₂} values for batch tests containing no detergent ranged from 32 to 224, with an average value of 126. K_{CO₂} values for batch tests containing an average of 25 mg/L detergent ranged from 1.52 to 3.60, with an average value of 2.57. The highest value for K_{CO₂} for any test occurred under conditions of approximately 1019 psi and 24°C with no detergent added (run #8). The lowest K_{CO₂} value for any test occurred under conditions of 1185 psi and 40°C with the addition of 28 mg/L detergent to the sample (run #23).

If NC/SCCO₂ extraction is to be considered as a viable method of extracting oil from bilge water containing detergents, further research will also be needed on methods of breaking surfactant micelles before or during the extraction process. Such methods might include chemical and/or co-solvent addition, addition of salts, or simply the elevation of temperatures and pressures significantly beyond those of the study.

Polynomial regression trend lines for batch group data series (best fit lines for K_{CO₂} values) for all batch groups showed curvature. In non-detergent tests, convex curvature occurred in best fit lines for near critical CO₂ at 25° and supercritical CO₂ at 39°C, while concave curvature occurred in the best fit line for supercritical CO₂ at 33°C. This may be due to the effects of increasing pressure and temperature on the density and solvating power of the CO₂. In detergent tests, convex curvature

occurred in best fit lines for supercritical CO₂ at 34° and 40°C, while concave curvature occurred in the best fit line for near critical CO₂ at 28°C. This may be due to the effects of pressure variation on the surfactant micelle, or possibly by the detergent mix used in this study should this mix contain ionic and nonionic detergents.

Best fit lines for K_{CO₂} values calculated using initial concentrations of oil paralleled best fit lines for K_{CO₂} values calculated using raw concentrations closely for all tests, but were greater in value since initial concentrations of oil were greater than raw concentrations of oil for each batch test.

Impeller mixing efficiency during the creation of oil/water emulsions (i.e. bilge water models) remained reasonably constant throughout the study, despite variations in initial oil concentration, amount of detergent, and temperature for batch tests. K_{CO₂} values were shown to increase only slightly in a 13 hour time period after raffinate sampling for detergent tests.

Continuing research should focus on how the NC/SCCO₂ extraction of oil from water and detergent/water solutions is affected by the following:

- higher temperatures and pressures
- extraction vessel impeller speed
- ratio of volume of carbon dioxide to volume of sample
- variance of the contact time between carbon dioxide and sample
- variance of the time allowed for carbon dioxide phase out after extraction (non-detergent tests).
- repeat extractions of the same sample with fresh CO₂ (as a simulation of a counter-flow reactor)

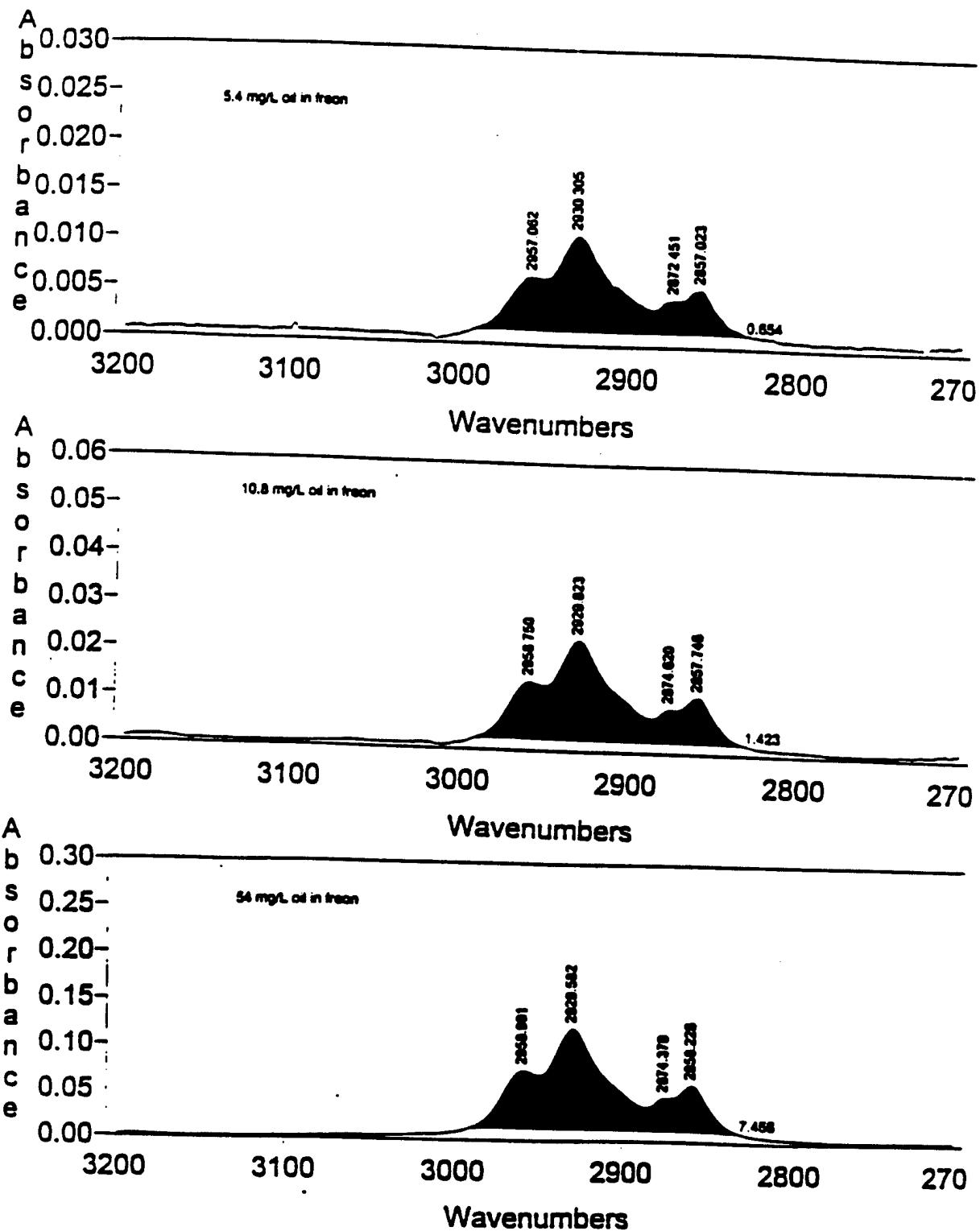
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Appendix A: Sample spectrograms from the standard curve run.



Appendix B: Freon extraction procedure of samples for FT-IR analysis.

Sample extraction was as follows:

1. 200 mL of sample was transferred to a 500mL separatory funnel. 15 mL of Freon was added to the empty sample bottle. The sample bottle was capped and shaken vigorously. The solvent from the sample bottle was then transferred to the same separatory funnel. The separatory funnel was then capped and shaken vigorously for 2 minutes.
2. Freon and water layers in the separatory funnel were allowed to separate. For samples containing detergent, approximately 1 gram of sodium chloride was added to enhance separation. The solvent extracted Freon was passed through solvent wetted filter paper in a glass funnel into a 50 mL volumetric flask.
3. Steps (1) and (2) were repeated two more times adding the 15 mL of clean Freon directly to the separatory funnel.
4. The Freon was brought to volume in the volumetric flask.
5. The water layer was drained into a graduated cylinder and its volume recorded (V_w).
6. For samples containing oil only, the Freon extract was then scanned by FT-IR. Concentration (A) was then determined from the calibration plot.
7. For samples containing detergent, the Freon extract was filtered with silica gel before being scanned by FT-IR. This consisted of placing 4 to 5 grams of washed silica gel in a filter paper inside a glass funnel. The extract was then drained through the silica gel into a clean glass beaker, and then scanned by FT-IR. Concentration (A) was then determined from the calibration plot.
8. Any samples giving results too high for the calibration curve were then diluted with Freon to within range.
9. Oil concentration in the sample (C) was calculated as follows:

$$C = A * 50 * DF / V_w \quad \text{where } DF = \text{dilution factor.}$$

Appendix C: Sample calculations for K_{CO_2} values.

Example: Run # 21

K_{CO_2} I C_i = initial concentration of oil = 477 mg/L
 C_f = concentration of oil in raffinate = 209 mg/L

$$\begin{aligned} K_{CO_2} &= \{(V_w / V_{CO_2}) * (C_i - C_f)\} / C_f \\ &= \{(1.98 \text{ L} / 0.9231 \text{ L}) * (477 \text{ mg/L} - 209 \text{ mg/L})\} / 209 \text{ mg/L} \\ &= 2.75 \end{aligned}$$

K_{CO_2} R C_i = concentration of oil in raw sample = 404 mg/L
 C_f = concentration of oil in raffinate = 209 mg/L

$$\begin{aligned} K_{CO_2} &= \{(V_w / V_{CO_2}) * (C_i - C_f)\} / C_f \\ &= \{(1.98 \text{ L} / 0.9231 \text{ L}) * (404 \text{ mg/L} - 209 \text{ mg/L})\} / 209 \text{ mg/L} \\ &= 2.00 \end{aligned}$$

Appendix D: Error analysis of batch testing and analytical procedures.

Volume : Batch Testing Procedure

The vessel volume (V_t) was measured to two different points. The vessel was first filled with D.I. water until a flat meniscus was observed at the top of the vessel. This volume was 2881.0 mL. Water was then added to the vessel to a point just before the meniscus expanded into the sealing-ring groove. This volume was 2925.2 mL (a difference of 44.2 mL). The average of the two was 2903.1 mL.

First measurement

H ₂ O addition method	tolerance	error
2 X 1000 mL volumetric flask	2 X 0.6 mL	1.2 mL
8 X 100 mL volumetric flask	8 X 0.16 mL	1.28 mL
81 mL from a 100 mL buret		0.2 mL

Second measurement

H ₂ O addition method	error
44 mL from a 100 mL buret	0.2 mL

$$\text{Difference between measurements} = 44 \text{ mL}; \text{ error} = 22 \text{ mL}$$

$$\begin{aligned}\% \text{ error} &= \{(\sum \text{ errors} + \text{diff. between measurements}) \div \text{avg. measurement}\} \times 100 \\ &= (24.88 \text{ mL} / 2903.1 \text{ mL}) \times 100 = 0.9\%\end{aligned}$$

Sample size (V_{H2O}) was measured in the following way:

H ₂ O addition method	tolerance	error
1 X 2000 mL volumetric flask	1 X 1 mL	1 mL
2 X 100 mL graduated cylinder	2 X 0.6 mL	1.2 mL

$$\begin{aligned}\% \text{ error} &= \{(\sum \text{ errors}) \div \text{sample volume}\} \times 100 \\ &= (2.2 \text{ mL} / 2200 \text{ mL}) * 100 = 0.1\%\end{aligned}$$

Volume of CO₂ used (V_{CO_2}) was affected by valve line drain out and raw sampling as follows:

sampling method	tolerance	error
1 X 20 mL beaker	1 X 4 mL	4 mL
2 X 100 mL graduated cylinder	2 X 0.6 mL	1.2 mL

Appendix D (continued)

$$\begin{aligned}\% \text{ error} &= \{(\sum \text{ errors}) \div \text{volume of CO}_2\} \times 100 \\ &= (5.2 \text{ mL} / 923.1 \text{ mL}) * 100 = 0.6 \%\end{aligned}$$

Total % error for the batch testing procedure (volume) = $(0.9 + 0.1 + 0.6)\% = 1.6\%$.

Volume: Sampling and Analytical Procedure

Sampling error is represented by:

sampling method	tolerance	error
2 X 100 mL graduated cylinder	2 X 0.6 mL	1.2 mL

$$\% \text{ error} = (1.2 \text{ ml} / 200 \text{ ml}) * 100 = 0.6\%$$

Errors in analytical procedure are represented by:

procedural step	method	tolerance	error
final volume of sample	2 X 100 mL graduated cylinder	2 X 0.6 mL	1.2 mL
final volume of Freon	50 mL volumetric flask	1 X 0.2 mL	0.2 mL
dilution of Freon (if needed)	3 X 10 mL volumetric pipet 2 X 5 mL volumetric pipet	3 X 0.02 mL 2 X 0.01 mL	0.06 mL 0.02 mL

$$\begin{aligned}\% \text{ error} &= \text{final volume of sample error} + \text{final volume of Freon error} \\ &= (1.2 \text{ mL} / 200 \text{ mL}) \times 100 + (0.2 \text{ mL} / 50 \text{ mL}) \times 100 \\ &= 1 \%\end{aligned}$$

$$\% \text{ error} (\text{with dilution factor}) = 1 \% + ((0.07 \text{ mL} / 40 \text{ mL}) * 100) = 1.2\%$$

Total % error for sampling and analytical procedure (volume) =

$$\begin{aligned}&\text{sampling error} + \text{analytical procedure error} \\ &= 0.6 \% + 1 \% = 1.6 \% \text{ (samples with no dilution factor) or} \\ &= 0.6 \% + 1.2 \% = 1.8 \% \text{ (samples containing a dilution factor)}\end{aligned}$$

Appendix D (continued)

Concentration

114 samples were analyzed by FT-IR for this study (not including the standard curve). These consisted of 92 samples, 17 blanks, and 5 standards. On average, a standard was run every 18 samples, and blanks were run every 5 samples. Standards deviated from predicted values on average 1.5%. The maximum a standard deviated from predicted value was 1.9%. The standard curve was prepared by making a stock standard solution of 500 mg/L and then diluting the stock to various concentrations using 100 mL volumetric flasks and varying volumetric pipets. The stock was prepared by adding 100 mg of oil (gravimetric method, Sartorius balance) to 200 mL of Freon. Each standard on the standard curve contains an error represented by:

procedural step	method	tolerance	error
weight of oil (stock standard)	gravimetric	1 mg / 100 mg	1%
volume of stock	200 mL volumetric flask	1 X 0.2 mL	0.2 mL
dilution of stock	volumetric pipet		0.2 % (max.)
volume of standard	100 mL volumetric flask	1 X 0.32 mL	0.32 mL

$$\begin{aligned}\% \text{ error} (\text{standards from standard curve}) &= \text{stock standard error} + \text{standard error} \\ &= (1 \% + 0.1 \%) + (0.2 \% + 0.3 \%) = 1.6 \%\end{aligned}$$

$$\begin{aligned}\text{Total \% error for concentration} &= \\ &\text{maximum standard deviation from predicted value} + \% \text{ error of standard} \\ &= 1.9 \% + 1.6 \% = 3.5 \%\end{aligned}$$

The total error for each calculation of K_{CO_2} would then be

$$\begin{aligned}&\text{total \% error for batch testing procedure (volume)} \\ &+ \text{total \% error for sampling and analytical procedure (volume)} \\ &+ \text{total \% error (concentration).}\end{aligned}$$

For samples not requiring Freon dilution, this would be

$$1.6 \% + 1.6 \% + 3.5 \% = 6.7 \%$$

For samples requiring Freon dilution, this would be

$$1.6 \% + 1.8 \% + 3.5 \% = 6.9 \%$$

Since all K_{CO_2} values incorporate raw concentrations, all error bars will be 6.9%

APPENDIX B: SUMMARY OF COLUMN DESIGN ANALYSES

An approach to sizing columns for extraction processes is the Height of Transfer Unit / Number of Transfer Units (HTU/NTU) method. As indicated by Cornell et. al. (1960) "The use of packed columns for continuous contacting of vapors and liquids is well established in the chemical industry." The HTU method is "a desirable and established practice..."

A common application of packed columns is air stripping of organic materials from contaminated wastewater (Lagrega et. al., 1994). Since counterflow NC/SCCO₂ extraction for water treatment is a relatively new technology, no HTU correlations exist. For this reason, it was decided to apply HTU predictions derived for air stripping operations. This was justified on the basis of a number of similarities between the two processes, e.g.;

- A. In each case, the contaminated water forms a continuous phase in the column, flowing downward.
- B. The extraction medium (NC/SCCO₂ or air) is the dispersed phase, and flows upward because its density is less than that of the contaminated water.
- C. The viscosity and surface tension of the dispersed phase are considerably smaller than that of the water, while the diffusivity of the contaminants is significantly higher in the extraction medium than in the aqueous phase. These factors combine to make diffusion through the water the dominant factor in the rate at which the (water/extraction medium/contaminant) system approaches equilibrium. The governing mass transfer coefficients should therefore be relatively independent of the extraction medium.

Despite these similarities, the physical properties of carbon dioxide (i.e. viscosity, surface tension, density and diffusivity) are closer to those of water than air. For this reason, the analyses discussed below are approximations at best.

To determine the number of transfer units required to effect a given level of treatment, we can use a McCabe-Thiele graphical analysis, or assuming linear partition behavior (Damle and Rogers, 1990)

$$NTU = \frac{R}{R-1} \cdot \ln \left[\frac{\left(\frac{C_{\text{raw}} - \frac{y_2}{m}}{C_{\text{raffinate}} - \frac{y_2}{m}} \right) \cdot (R-1) + 1}{R} \right]$$

Where;

- R = Stripping factor (CO_2 flowrate vs. equilibrium flowrate)
- m = Slope of "equilibrium line" ($= K_{\text{CO}_2}$)
- $C_{\text{raw/raffinate}}$ = Inlet and outlet (target Raffinate) oil concentrations
- y_2 = Concentration of oil in inlet CO_2

The height of a transfer unit is a complex function of a number of geometrical and transport properties, as summarized in the following table;

Table B.1: Parameters in HTU Calculations

Fluid Parameters	Densities	$\rho_L, \rho_{\text{CO}_2}$
	Viscosities	μ_L, μ_{CO_2}
	Diffusivities	D_L, D_{CO_2}
	Schmidt Number	Dimensionless combinations of the above
Packing Parameters	Critical Surface Tension	σ_C
	Surface Area	a_t
	Wetted Surface Area	a_p
	Diameter	d_p
Process Parameters	Liquid Loading	L
	Stripping Medium (CO_2) Loading	G

A number of HTU correlations were applied in order to generate preliminary estimates of column height for a 10 gpm shipboard. Although a wide range of published HTU data is available, efforts were made to identify and apply those correlations that explicitly take into account the physical properties of the fluid media.

As an example, consider the expressions developed by Onda et. al. (1968), which are summarized below;

$$k_L = \left(\frac{\rho_L}{\mu_L g} \right)^{-\frac{1}{3}} \cdot 0.0051 \cdot \left(\frac{L}{a_w \mu_L} \right)^{\frac{2}{3}} \cdot Sc_L^{-\frac{1}{2}} \cdot a_t d_p$$

$$k_G = a_t D_G \cdot 5.23 \cdot \left(\frac{G}{a_t \mu_G} \right)^{0.7} \cdot Sc_G^{\frac{1}{3}} \cdot \frac{1}{(a_t d_p)^2}$$

$$\frac{a_w}{a_t} = 1 - \exp \left[-1.45 \cdot \left(\frac{\sigma_c}{\sigma_w} \right)^{0.75} \cdot \left(\frac{L}{a_t \mu_L} \right)^{0.1} \cdot \left(\frac{L^2 a_t}{\rho_t^2 g} \right)^{-0.05} \cdot \left(\frac{L^2}{\rho_L \sigma a_t} \right)^{0.2} \right]$$

$$\frac{1}{K_{OVERALL} a} = \frac{1}{K_{CO_2} k_G a} + \frac{1}{k_L a}$$

$$HTU = \frac{L}{K_{OVERALL} a}$$

In addition to these equations, similar HTU correlations developed by Cornell et. al. (1960) and Shulman et. al. (1955) were applied, with fairly consistent results. Values derived using the method of Sherwood and Holloway (1940) were not in agreement.

While the HTU/NTU method is used to predict the required column height for a given flowrate and contaminant concentration, the column diameter is governed by the need to operate at "unflooded" conditions. McCabe et. al. (1985) describe the flood point for liquid/liquid extraction as the condition under which "... the dispersed phase coalesces, the hold-up of the phase increases, and finally both phases leave together through the continuous-phase outlet." In air-stripping operations, flooding is described as the conditions in which the air flow is great enough to "... hold back the free downward flow of water.." (LaGrega et. al, 1994).

Perry and Green (1984) present a generalized correlation for flooding as a graphical relationship (see Figure B.1) between two dimensionless parameters (one related to the gas and liquid velocities and densities, the other incorporating packing parameters and liquid viscosity). McCabe et. al. present a similar graph for liquid/liquid extraction (Figure B.2).

Figure B.1: Generalized Flooding Correlation (Perry and Green, 1984)

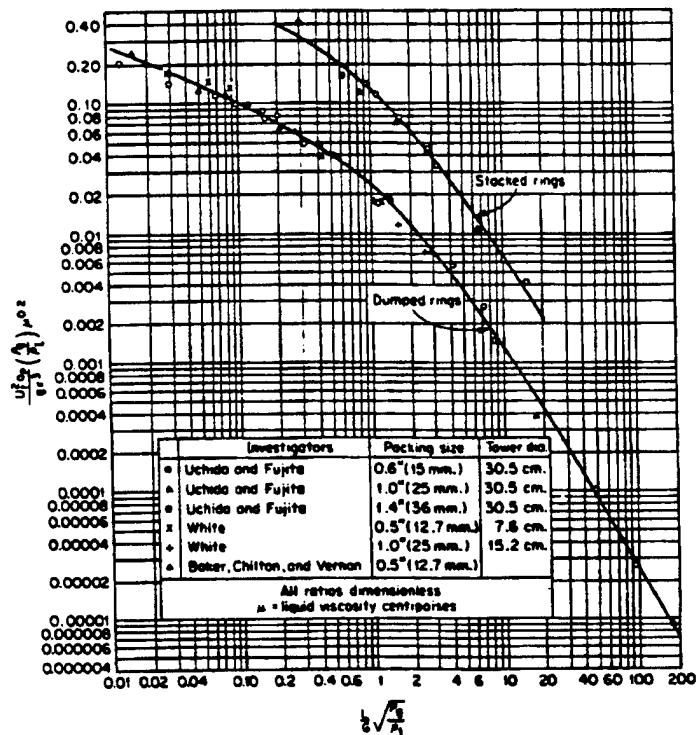
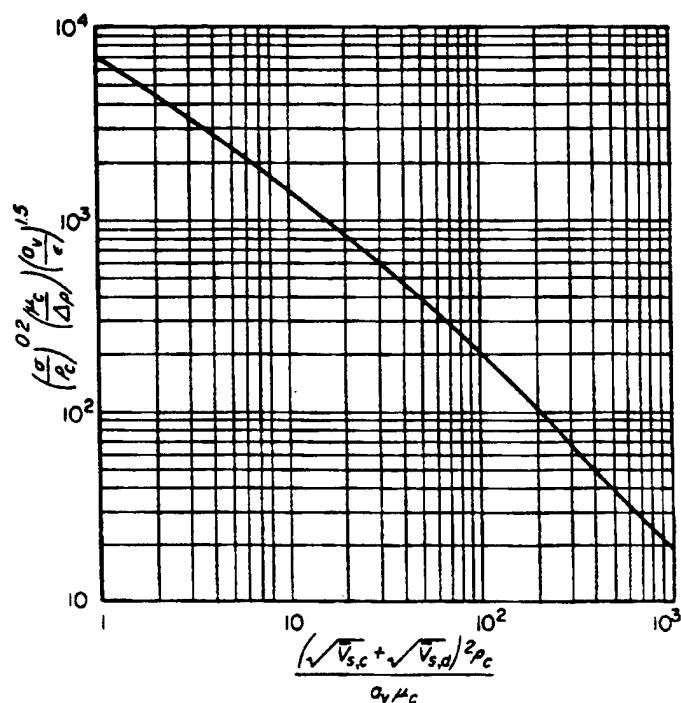


Figure B.2: Flooding Velocities in Packed Extraction Towers (McCabe et. al., 1985)



Several NTU/HTU correlations and the flood point correlations shown in Figures B.1 and B.2 were implemented in a Mathcad spreadsheet, which allows all parameters to be varied to evaluate different operating conditions. Table B.2, below, summarizes results for the target 10 gpm flowrate, as well as for two smaller (laboratory scale) systems. Additional analyses with varied parameters can be easily performed using this tool.

Table B.2.A: Assumptions for all Analyses

Additive	36% seawater to give approximate 1% NaCl concentration
Inlet oil concentration	500 ppm
Effluent concentration	5 ppm
Partition Coefficient (K_{CO_2})	100
Stripping factor (ratio of CO_2 flow to equilibrium flow - usually ranges from 2 to 10 per LaGrega et. al.)	5 - Intermediate value
Packing	½" Polyethylene Berl saddles, dumped

Table B.2.B: Results for Specific Cases

Flowrate	Column Construction	Height (Onda)	Height (Cornell)	Factor of Safety (Based on Yield Point Stress)
10 gpm	14" sch. 10 pipe (steel)	9.9'	13.6'	3.5
10 gpm	16" sch. 40 pipe (steel)	8.8'	16.6'	6.1
1 gpm	6" sch. 40 pipe (304 stainless)	6.7'	9.2'	3
0.25 gpm	3" sch. 40 pipe (304 stainless)	6.6'	6.5'	4.5

As shown in Table B.2, predicted column heights are fairly consistent. Assuming that we pick a conservative column height of 15' and increase this by approximately 50% to provide a margin of error, a realistic shipboard 10 gpm column would consist of four six foot tall tubes (joined in series) each constructed of 16" schedule 40 alloy steel pipe. This contrasts with the earlier predictions of a 118' column. Table B.3 gives updated weights and volumes for a shipboard system.

Table B.3: Estimates of Column Size for Nominal 10 gpm Shipboard System

Parameter	Earlier Analysis Reported June, 1998	Present Analysis
Column Height	120' (20 x 6' long pipes in series)	24' (4 x 6' long pipes in series)
Column OD and Wall Thickness	10.75" x 0.25"	16" x 0.5"
Column Weight	3400 lb	2000 lb
CO ₂ Recovery System, Condensers, etc.	4900 lb	4900 lb
Water in Column and Blowdown Tank(s)	5800 lb	3300 lb
Total Weight	14,100 lb	10,200 lb
Pallet Size	100" x 100"	Some size reduction Possible, but limiting Factor may be compressor(s) and condenser(s).

APPENDIX C: BIBLIOGRAPHY

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